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Fig. 1. Side view.

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Fig. 2. Rear view, showing spring opposed jaws.

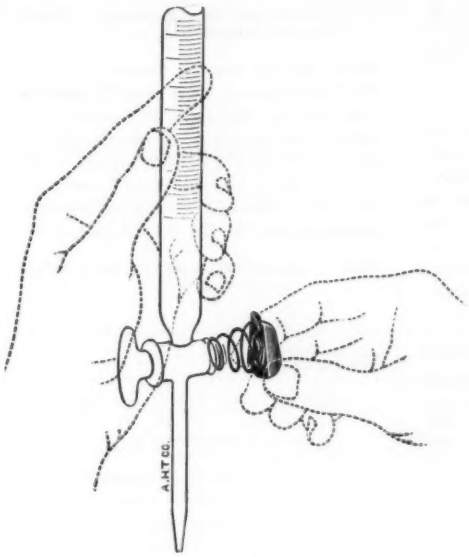

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Fig. 3. Showing method of attachment or removal.

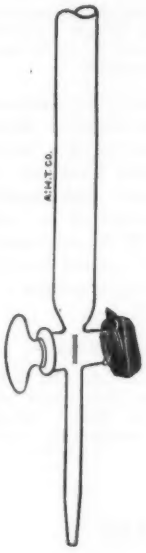

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Fig. 4. In position.

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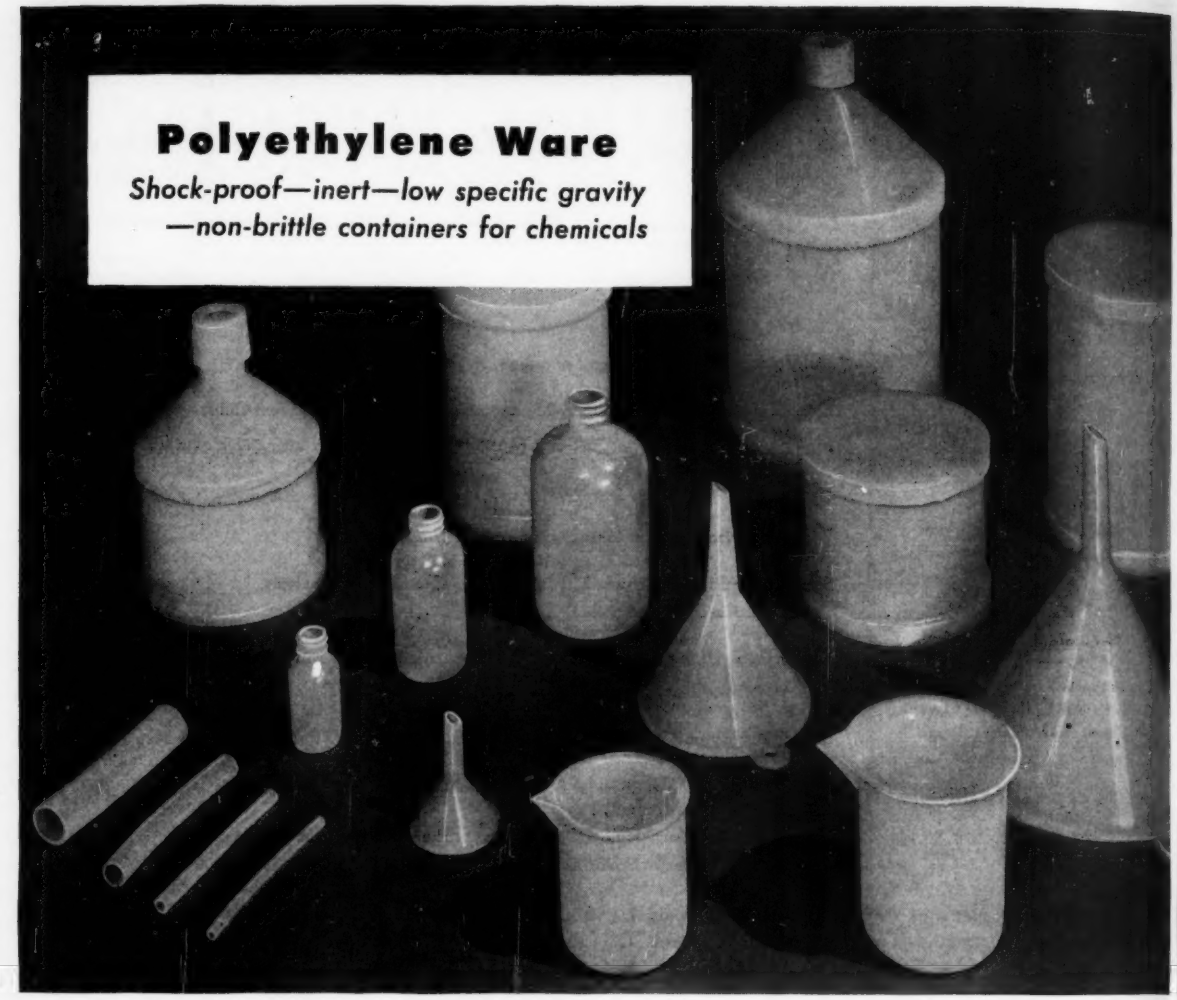

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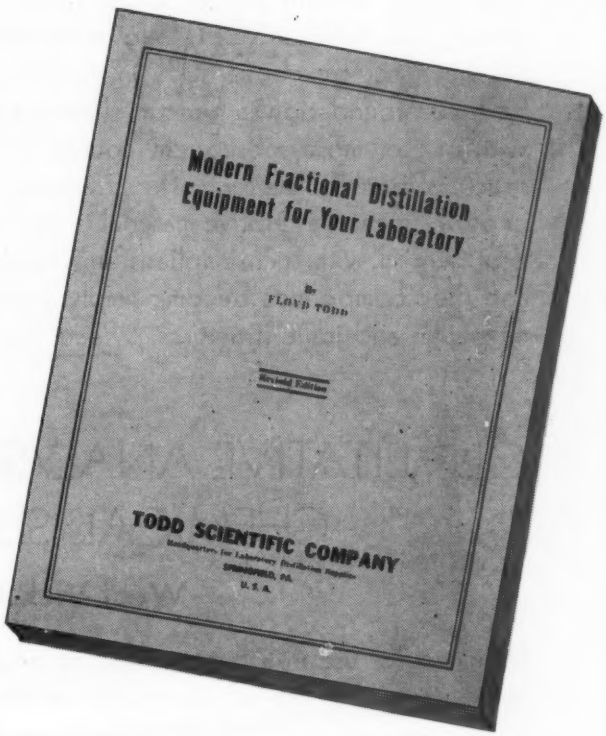

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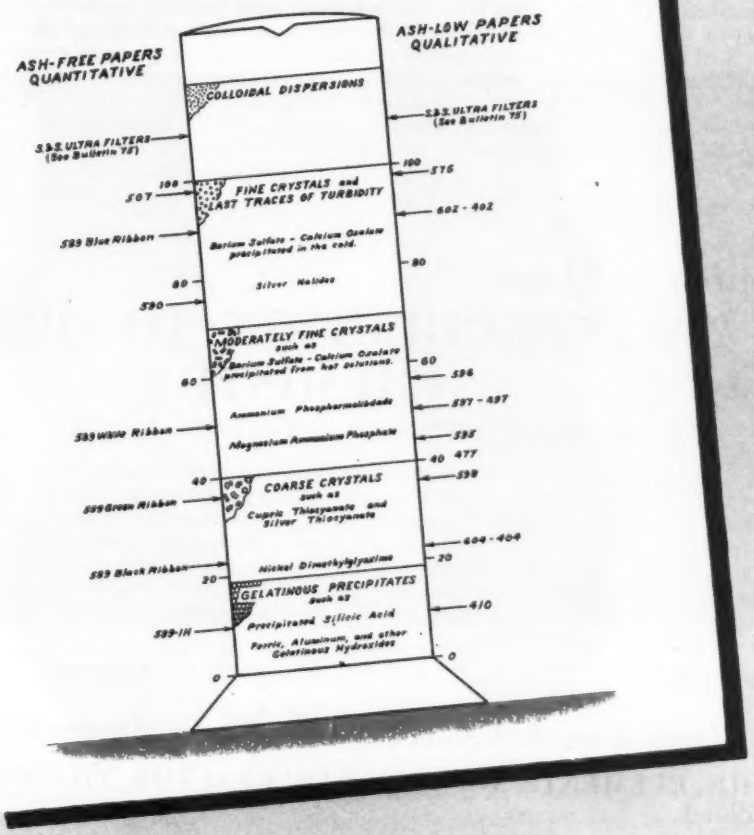

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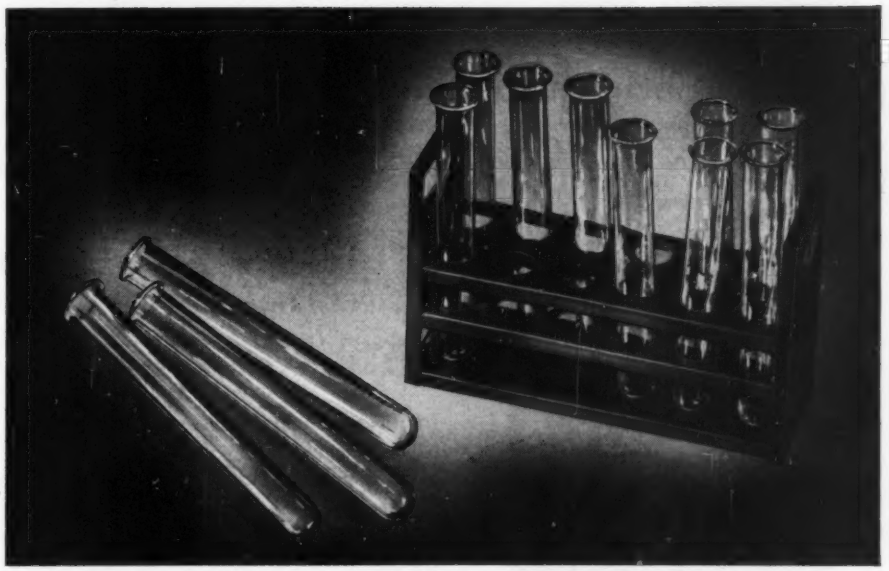

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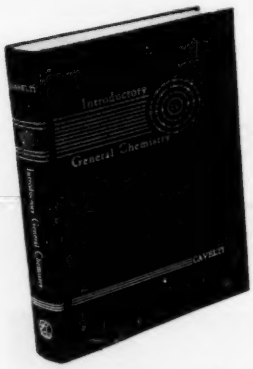

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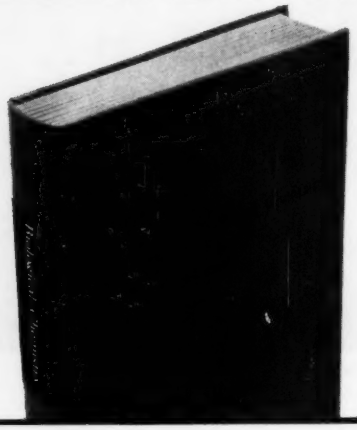

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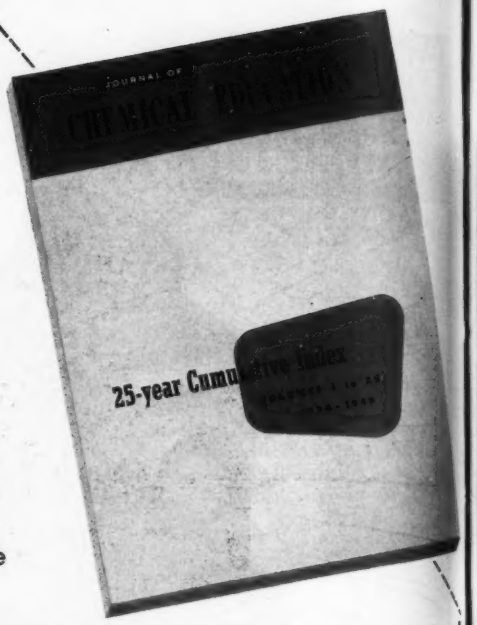

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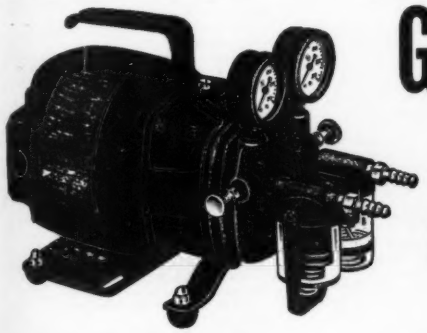

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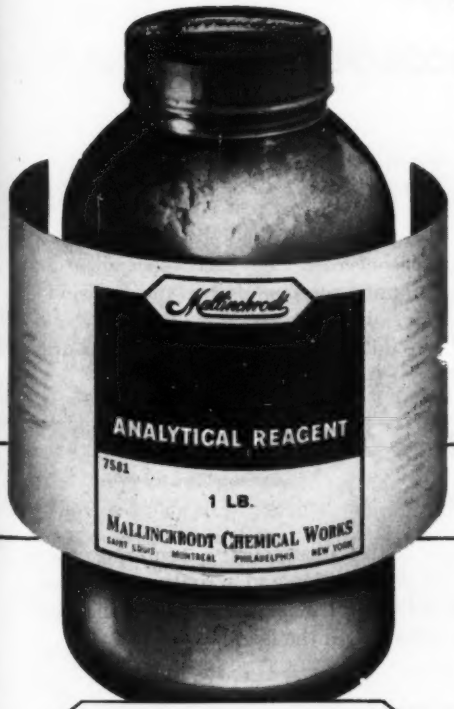

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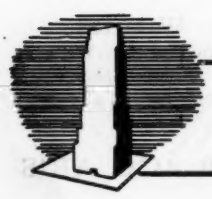

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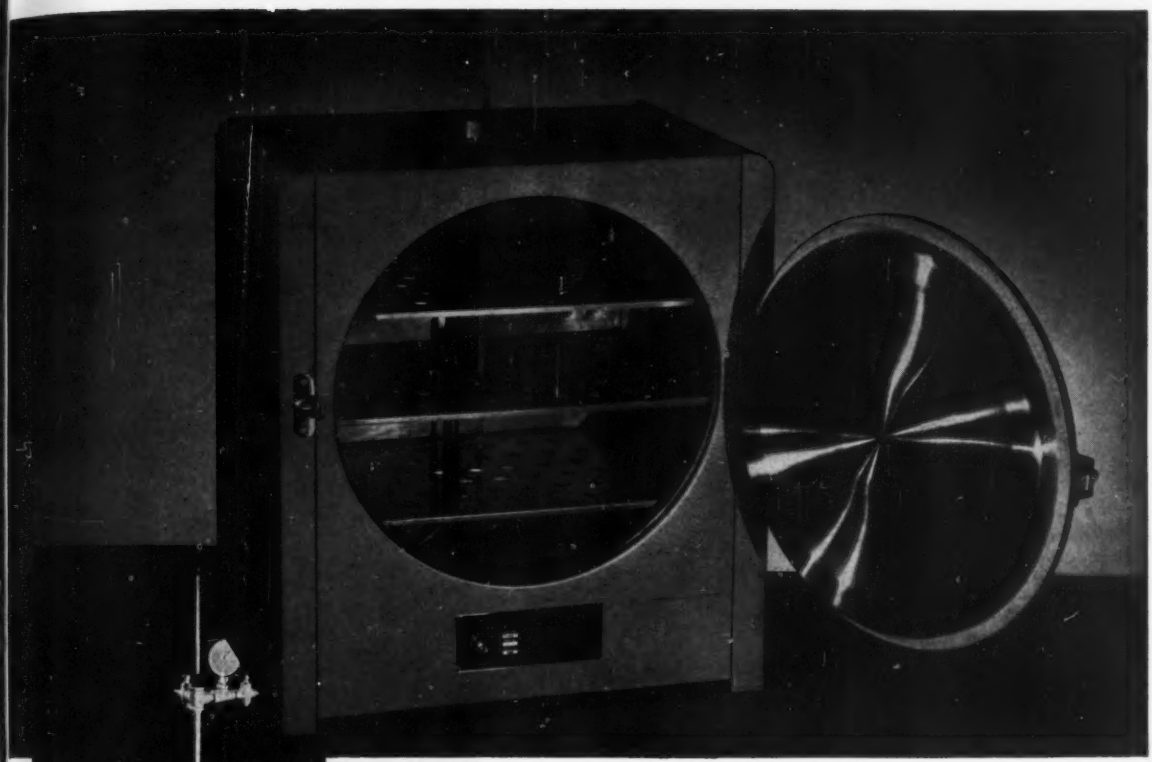

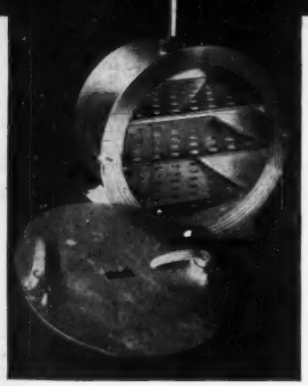

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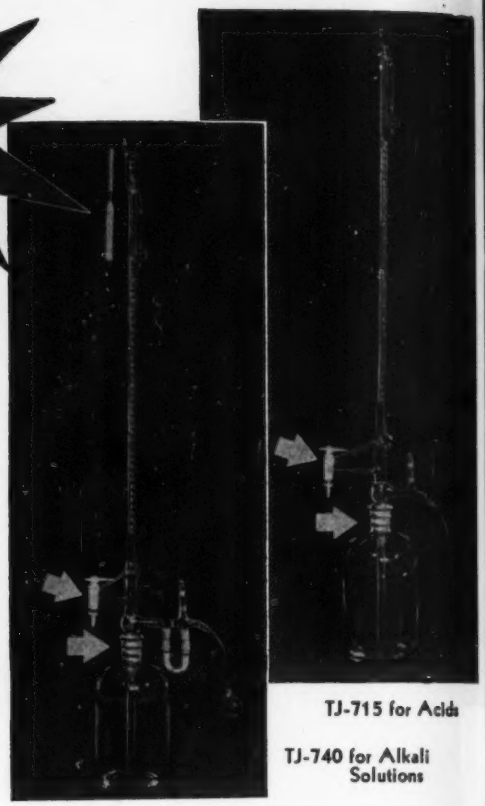

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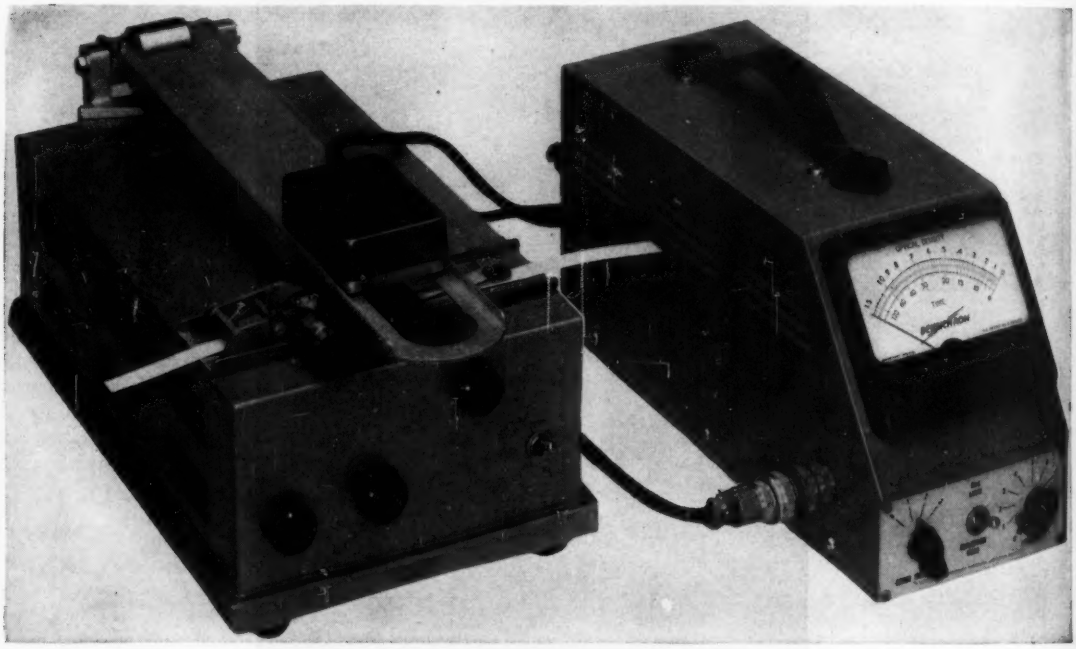

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Editor's Outlook

In our issue of September, 1952, we carried a short biographical sketch of Burckhardt Helferich. It was interesting to come across an address by him on the general subject of chemical education, published in a recent number of *Die Naturwissenschaften* ["Chemie und Schule," **39,** 537 (Dec., 1952)].

Some of his remarks are worth reviewing although it would probably be hard to find anything radically *new* to say about this subject. (I can hear someone ask why we should continue to publish this journal!) But whether new or not, it is interesting to observe the emphasis placed upon well-known factors by a person in a rather different scholastic environment.

Of course, he dwells upon the strategic place of chemistry in the affairs of the present-day world. He extols the value of chemistry in general education, insisting that everyone who passes through the higher schools whether or not he is later to become a professional chemist, should get a thorough grounding in the principles of chemistry. For the training of the chemist himself, he does not neglect to point out the necessity of foreign languages (English and French), physics, biology, and particularly mathematics.

For satisfactory results in the teaching of chemistry a properly equipped laboratory is necessary, where the teacher can carry out demonstrations and where students—at least in small groups—can themselves conduct experiments. Such equipment costs money but it must be found.

Particular emphasis is put upon the necessity for thorough preparation of the chemistry teacher. He must master his own science if he is to be able to give his pupils a proper understanding and appreciation of it. Furthermore, he must keep up with the advances of his science. He cannot rest upon such laurels as he may have won during his period of training; he must keep up to date. This is not as easy in chemistry as it is in some of the other subjects, and in order to do so, the teacher must be given time and facilities for self-improvement. He suggests occasional "teachers' courses," even though these may need to be subsidized. To this end, also, chemistry teachers must not be overloaded with other subjects.

He also makes a plea for modern textbooks, which must not be kept in use until they are long out of date. (On this score, I wonder if German practice is any better—or worse—than American!)

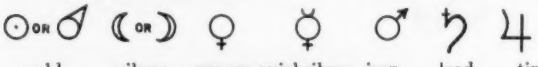
Finally he comes to what the present-day radio public will recognize as "the sixty-four-dollar question"—how to recruit and retain good chemistry teachers. His answer may not be any different from ours, but it is well stated: "Talented young men can only be attracted to the teaching profession if the profession is worth striving for." In addition to such attractions as the joy of teaching and the association with young, growing minds, there must also be a recognition of some of the hard facts of everyday life—the necessity for adequate salaries and for the time and the material required for teaching and for self-improvement.

All of this will have a familiar ring to teachers in this country, too. The problems of chemical education are not local, but international.

HISTORY OF THE CHEMICAL SIGN LANGUAGE

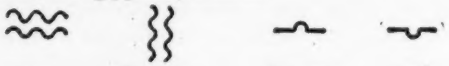
RUDOLF WINDERLICH*
Oldenburg im Oldenburg, Germany
(Translated by Ralph E. Oesper)

THE earliest chemical symbols dealt only with the seven metals known to the ancients. Though they were not uniform among all writers, they usually agreed with the primary symbols of the deities and planets with which they were associated:



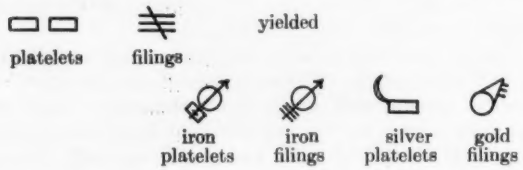
gold sun | silver moon | copper Venus | quicksilver Mercury | iron Mars | lead Saturn | tin Jupiter

They served probably only as abbreviations. Gradually others were added, but it cannot be established with certainty when and where this accretion occurred. These newcomers included symbols for substances, measure and weight, and finally they included signs for many words in daily use. In part they came from Egyptian hieroglyphics, such as:



water | rainwater | heaven | earth

The list was constantly increased in the alchemical literature. These signs made the texts unintelligible for the laymen, but they aided the adepts because the symbols were logically combined into larger units. For example:



platelets | filings

iron platelets | iron filings | silver platelets | gold filings

However, since the alchemical writers continuously invented new symbols for themselves and their students without regard to others in the profession, eventually there arose such confusion that after Greek alchemy reached its full height the succeeding generations found it necessary to assemble lists of the signs employed in order to read the famous old works of their masters.

Zuretti[1] published lists constructed from the most important codices. He explains the origin and meaning of the various symbols to a great extent, and thus facilitates the reading of alchemical texts. Ruska[2] continued the study of the origin and relation of the various symbols. He dealt with the symbols of Greek alchemy, the forms of the Syrian signs, and the origin of the newer chemical symbols of the lexicon by Sommerhoff.[3]

The various lists were not put out by practicing alchemists; rather, we owe them to philologically trained compilers and copyists. The Latin translations contain "whole lines with new symbols." We do not know where these came from, but in any case they bear no relation to Greek signs. Sommerhoff's "Lexikon" shows how necessary the lists were, since he gives 14 different symbols for *acetum* (*i. e.*, vinegar) and no less than 37 for *aurum* (gold).

Johann Joachim Becher (1635–82) was the first to issue a selection of signs in the form of a table. This contained ten groups, namely: *minerae, metalla, minerales, salia, decomposita, terrae, distillata, olea, limi, compositiones.* This venture was not very successful. In 1718 Geoffroy the Elder (1672–1713) published his famous "Table of Affinity."[4] His object was to give the students ". . . en peu de temps une juste idée du rapport que les différents substances ont les unes avec les autres" and to provide the experienced chemists with a means of determining at a glance what occurs in many of their operations which are difficult to fathom.[5] The first line of the table (Figure 1) contains different substances, which are frequently employed in chemistry. Beneath each of these are several materials placed in different columns according to decreasing affinity—without regard to temperature, etc.—the arrangement being such that the nearest substance has the greatest affinity to the material at the head of the column. The first column is labeled "esprits acides," of which Geoffroy knew three: hydrochloric, nitric (actually nitrogen oxides), and sulfuric (actually sulfur dioxide). With respect to their behavior toward the metals "SM," the acid spirits appear again at the top of the second, third, and fourth columns. Directly below "vitriolic acid" is the *principe huileux ou soufre principe* (which is nothing other than phlogiston), and in modern terms this means that SO_2 is oxidized to SO_3. Geoffroy

* Died July 15, 1951.

[1] ZURETTI, C. O., "Alchemistica Signa digessit et explanavit." Secretariat Administratif de l'Union Académique Internationale, Brussels, 1932.

[2] RUSKA, JULIUS, "Neue Beitrage zur Geschichte der Chemie," Parts II to IV, *Quellen und Studien zur Geschichte der Naturwissenschaften und der Medizin*, Vol. 8, Parts 3 and 4, Berlin, 1942.

[3] SOMMERHOFF, J. C., "Lexikon Pharmaceuticochymicum Latino Germanicum," Nürnberg, 1701.

[4] "Table des différents rapports observés en chimie entre différents substances," *Memoires de l'Académie Royale*, Paris, 1718. Amsterdam reprint 1723, pp. 256–269.

[5] For a likeness of Geoffroy, see THIS JOURNAL, 13, 101 (1936).

retained the old symbols for the metals, *i. e.*, the solar disc for gold, the crescent moon for silver, the Venus mirror for copper, the shield and spear of Mars for iron, the scythe of Saturn for lead, the throne or sceptre of Jupiter for tin, mirror and crescent moon for Mercury. It is noteworthy that the heavenly bell was retained for all the volatile acids, obviously because they travel toward the celestial regions.

The chemists doubtless derived great use from the table, both because of its symbols and its survey of affinities. For instance, P. J. Macquer (1718–84) took it over unchanged in his widely used "Éléments du chymie théorique," and O. T. Bergman (1735–84) improved and considerably extended it in his "De attractionibus electivis" published at Uppsala in 1775.

C. W. Scheele always used the short-cut symbols in his laboratory notebooks. In 1777 (perhaps as early as 1769) he described the preparation of oxygen: "☿ rubr. ♌ yielded much 🜁🜂🜄, no 🜁 fix, very little ♒ yellow reddish and ☿ viv." Transcribed: "*Mercuris precipitatus ruber* on distillation gave much vitriolic air, no fixed air, very little yellow reddish sublimate and *mercurium vivum*," or in modern terms: "On heating red mercury calx there resulted much vitriolic air,[6] no carbonic acid gas, very little of a yellow reddish sublimate and liquid mercury."[7]

Lavoisier sought to express *quantitative* relationships by the symbols which came down to him and by the few which he invented; in order "d'appliquer l'exactitude du calcul à la chimie."[8] He was well aware that he was still far from this goal.[9] In one trial he found that 0.2000 livres of "chaux de fer" contained 0.200 livres of iron ♂ and 0.058 livres "principe oxygène ✣," which agrees fairly well with FeO.

J. H. Hassenfratz (1755–1827) and P. A. Adet (1763–1832) tried to give chemical notation a uniform and clear form in 1787. They used simple geometrical characters. In their scheme, oxygen was represented by a horizontal stroke —, nitrogen by /, hydrogen by a semicircle), carbon similarly by (, sulfur by ⌣, and

[6] That is, oxygen, which Scheele had prepared earlier by heating sulfuric (vitriolic) acid with pyrolusite.

[7] "Nachgelassene Briefe und Aufzeichnungen," edited by Nordenskiöld, Stockholm, 1892, p. 458. SCHEELE, C. W., "Manuskrupt 1756–1777," Uppsala, 1942, vol. I, p. 107. Scheele used no symbols in his publications which appeared during his lifetime.

[8] "Considérations générales sur la dissolution des métaux dans les acides," *Mém. Ac. Paris*, 1782 (published 1785), pp. 492–511.

[9] ". . . we are still quite far from being able to bring mathematical precision into chemistry and consequently I request that the formulas which I have given you be considered only as simple annotations, whose object is to lighten the operations of the mind." Lavoisier, *op. cit.*, p. 499.

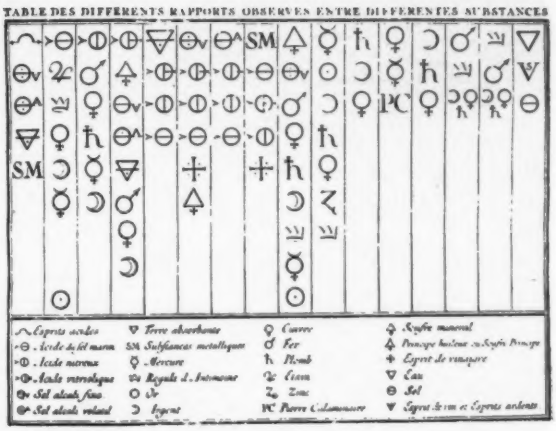


Figure 1

phosphorus by ⌒. The metals were designated by letters enclosed in circles, *e. g.*, (Fe) *ferrum*, iron, (C) *cuprum*, copper, (P) *plumbum*, lead, (S) *stannum*, tin, (Sb) *stibium*, antimony. Squares were similarly used for acids, *e. g.*, [M] *acidum muriaticum*, hydrochloric, [A] *acidum acetum*, acetic. Alkalies and earths were represented by triangles, *e. g.*, (P) potash, (S) soda, (C) lime, (B) baryta, (M) magnesia. Even though their suggestions were recommended by a committee of the Academie,[10] the new notation was not favorably received because the characters did not lend themselves to fluid writing.

John Dalton, the reviver of the atomic theory, took the next step.[11] He employed circles with inserted markings to indicate the elements (see Figure 2). Compounds were represented by placing the symbols for the particular elements side by side. For instance:

carbon monoxide — carbon dioxide — nitrous gas — nitrous oxide

The assemblage of small circles gave a picture of the qualitative and the quantitative composition of the compound.

However, despite the logical *quantitative* representations, Dalton's symbols did not gain acceptance because they were too cumbersome. They lived out their existence within the confines of his laboratory journals. The great Swede, J. J. Berzelius (1779–1848) helped the situation with one great stroke; he simply replaced the circles with the beginning letters of the names of the elements, and indicated the number of atoms of each

[10] "Rapport sur les nouveaux charactères chimiques," Lavoisier, "Oeuvres," V, Paris, 1892, pp. 365–375.

[11] "New System of Chemical Philosophy," Manchester, 1808. The first public statement of his ideas was in a lecture delivered to the Literary and Philosophical Society of Manchester on October 21, 1803.

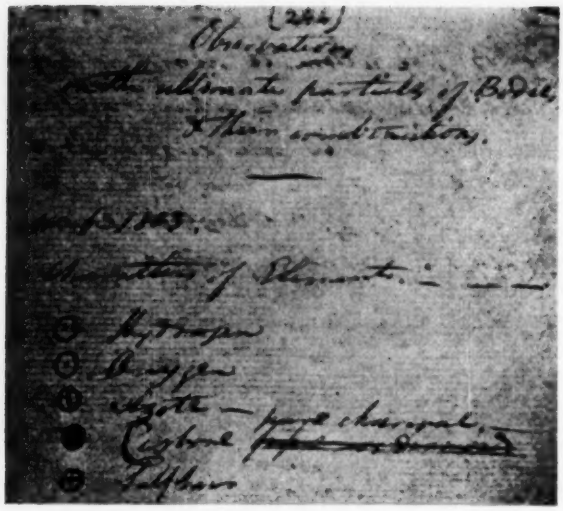


Figure 2

of the particular elements by an exponent-like superscript, *e. g.*, SO^5. In this symbolism, the letters (S) represented not only the elemental material as such, but also, following Dalton's lead, the relative atomic weight.[12] The indication in the title: ". . . method of employing them to express chemical proportions" characterizes the essence of the matter.

With reference to his proposals, Berzelius remarked: "I must observe here that the object of the new signs is not that, like the old ones, they should be employed to label vessels in the laboratory; they are destined solely *to facilitate the expression of chemical proportions*, and to enable us to indicate, without long periphrases, the relative number of volumes of the different constituents contained in each compound body. By determining the weight of the elementary volumes, these figures will enable us to express the numeric results of an analysis as simply, and in a manner as easily remembered, as the algebraic formulas in mechanical philosophy." Actually, no memory would be capable of remembering the percentage composition of a large number of compounds, whereas it is easy to memorize the few atomic weights and the most important formulas from which the percentage composition can be calculated at any time.

The objections advanced by his critics were repeatedly refuted by Berzelius in his *Jahresberichte*. For example, he cogently remarked: "I agree with Mr. Brande that nothing can be put into a formula which could not be also expressed by words, and that in case these words expressed the thought just as easily as the formula, then the use of the latter would be foolish. However, there are instances where this is not true, and in which the formula states at a glance what if put into words would have required several lines, and where the expression by the formula is clearer and more readily understood by the reader than the lengthy description with words."[13]

His initial proposal of 1814 in which he simply used letters, was later modified in two respects. At first he employed special signs for oxygen, and then also for sulfur, selenium, and tellurium, when they were included in compounds. Oxygen was indicated by dots, sulfur by vertical and selenium by horizontal strokes, and tellurium by plus signs. For example: $\dot{C}$ (CO_2); $\dot{Zn}$ (ZnS); $\dot{K}\dot{M}\dot{o}$ (K_2MoO_4); $\dot{K}\dot{M}\dot{o}$ (K_2MoS_4); $\dot{K}\dot{M}o$ (K_2MoSe_4); $\dot{K}\dot{M}o$ (K_2MoTe_4). Moreover, he used a horizontal bar through the letter to represent the double atoms which he assumed to be present in many compounds; *e. g.*, $\dot{\overline{H}}$ (H_2O); $\dot{\overline{Al}}$ (Al_2O_3). These deviations from the simple basic ideas of the notation system were not retained by the chemical world because of possible misunderstandings, and furthermore, following the proposal of Liebig and Poggendorff, the custom was gradually established of writing the numbers as subscripts rather than as superscripts.

As the science progressed, Berzelius himself found it necessary to introduce suitable modifications in the formulas. His own indefatigable studies on the determination of the relative atomic weights forced him to do this. In 1826, when he published a new table of atomic weights,[14] he had already altered most of his earlier figures; he had divided them by 2 or 4, in order to bring them into harmony with the Dulong-Petit law of atomic heats and Mitscherlich's law of isomorphism; the formulas of the compound substance had to be fitted to these new values.

Even in his first outline of 1814, Berzelius considered the possibility of a regular relationship between the atomic weight and the volume occupied by an atom. Consequently, it is readily apparent that Dumas' classic vapor-density determinations made a deep impression on the author of the chemical symbolism, since they offered a solution of this problem. "We have long assumed that the atomic weights of substances and their volumes in the gaseous state will be expressed by the same relative number."[15] He was convinced "that in the gases of simple substances there was an equal number of atoms present in an equal volume." If in this statement he had been able to replace the expression "an equal number of atoms" by "an equal number of molecules," he would have announced the Avogadro theorem in the form in which it is now accepted, and thus would have saved himself and his contemporaries many difficulties. However, the time was not yet ripe for this. A proposal contained in a letter (September 5, 1839) sent to Berzelius

[12] The first announcement of the Berzelian notation appeared in January, 1814, in Thomson's *Annals of Philosophy:* "On the chemical signs and the method of employing them to express chemical proportions." The Swedish and German publication followed soon thereafter. See Schweigger's *Journal für Chemie u. Physik*, **13**, 240 (1815); compare also Gilbert's *Annalen*, **46**, 154 (1814), footnote; Thomson's *Annals*, **3**, 51 (1814).

[13] BERZELIUS, *Jahresbericht*, **4**, 119 (1824).

[14] *Poggendorff's Annalen*, **7**, 397 (1826); **8**, 1, 177 (1826).

[15] BERZELIUS, *Jahresbericht*, **13**, 59 (1834).

by Liebig is interesting in this connection "... we ought to make up our minds to see in our formulas the equivalents instead of atoms of the volume theory." It was not until the concepts of equivalent, atom and molecule were clearly differentiated through the studies by Charles Gerhardt and Auguste Laurent and the logical clarity of Cannizzaro's thinking, that it became possible to include weight and volume simultaneously in a single formula. Gerhardt, beginning in 1843, was the first to advocate the principle that the chemical formulas of all gasifiable material should be referred to equal volumes. Williamson's studies of the formation of ethers showed the expediency of this idea. Then Cannizzaro in his "Sunto di un corso di filosofia chimica," carried through the system of symbols in use today, showing that it expressed the known facts in the most concise form. The general acceptance was somewhat delayed because of the abnormal vapor densities of ammonium chloride and phosphorus pentachloride. But when it was proved that these materials dissociate on heating, the way was cleared and all obstacles removed. The facts acquired subsequently and the later methods of determining molecular weights—osmotic pressure, freezing point depression, boiling point elevation, periodic system, distribution of the spectral lines—have brought no significant change.

Berzelius had the rare gift of creating new and fruitful chemical concepts in which were brought together divergent conflicting items. His paper "On the composition of tartaric and racemic acid"[16] gave the impetus to an articulation of the chemical formulas. He proceeded from the fact that "racemic acid not only has the same atomic weight but also the same percentage composition as tartaric acid." He combined this knowledge with the results obtained by Liebig and Wöhler, whose accurate analyses of silver fulminate and cyanate, respectively, had yielded identical values, and likewise with Faraday's discovery that ethylene and butylene have the same percentage composition though their vapor densities are not alike, and with Wöhler's conversion of ammonium cyanate into urea. For these isolated facts he coined the comprehensive term "isomerism," in which he assumed that "an equal number of the same elements are combined with each other in a dissimilar fashion," whereas in polymerism the materials "having identical percentage composition possess unlike atomic weights, which usually are multiples of each other." In this way conclusive proof was produced that simple empirical formulas are not adequate, a conclusion which Berzelius later confirmed by stating: "otherwise it would be impossible to explain why acetic methyl oxide [CH_3COOCH_3] and formic ethyl oxide [$HCOOC_2H_5$] are absolutely different compounds."

The earliest usable combination of chemical formulas was due to Gerhardt. In his system based on the homologous series, he arranged the innumerable formulas according to types, of which he used four:

$$\left.\begin{matrix}H\\H\end{matrix}\right\}; \left.\begin{matrix}H\\Cl\end{matrix}\right\}; \left.\begin{matrix}H\\H\end{matrix}\right\}O; \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$$

By replacement of the individual members of these types with other elements or groups (radicals), all necessary formulas could be derived, *e. g.*, from $\left.\begin{matrix}H\\H\end{matrix}\right\}$ the homologous series

$$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}, \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}, \left.\begin{matrix}C_3H_7\\H\end{matrix}\right\}, \text{ etc.,}$$

or from $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ can be derived

$$\left.\begin{matrix}K\\H\end{matrix}\right\}O, \left.\begin{matrix}K\\K\end{matrix}\right\}O, \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O, \left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O, \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O, \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S, \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O,$$

$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O, \text{ etc.}$$

"If one-half of its hydrogen is replaced by a hydrocarbon group CH_3, C_2H_5, etc., the water type produces alcohol. If all of the hydrogen is substituted by a group of this kind, the corresponding ether results. If the same type exchanges one-half of its hydrogen for a group which contains both carbon and oxygen, a monobasic water-containing acid is produced. If both hydrogen atoms of water are replaced by the same group, the corresponding anhydrous acid results."[17]

August Kekulé added the $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}$ C type. Following Frankland's lead, he drew conclusions relative to the saturation capacity of the various elements, *i. e.*, to their valence. Through the concept of the replacement value or valence, the Gerhardt formulas took on a deeper meaning. In this same paper on the nature of carbon, Kekulé[18] also showed that "the carbon atoms themselves can combine with each other, whereby of course a part of the affinity of one is bound toward an equally large part of the affinity of the other." These findings and suppositions flowered into the struc-

[16] *Poggendorff's Annalen*, 19, 305 (1830).

[17] Gerhardt, C., *Ann. chim. phys.* [3] **37**, 285 (1853); *J. prakt. Chem.*, **61**, 268 (1854).

[18] Kekulé, A., *Ann.*, **106**, 129 (1858).

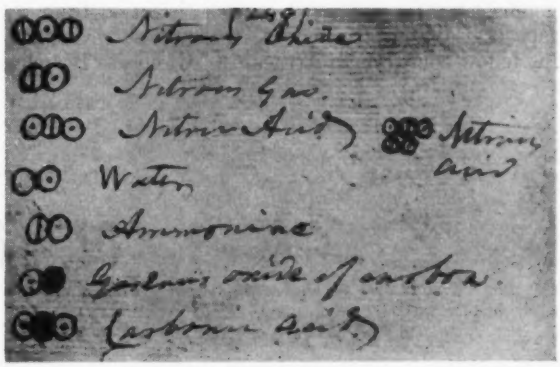


Figure 3

tural formulas of organic chemistry, which reached the peak of its expression in Kekulé's formula for benzene and its derivatives, and in the representations introduced by van't Hoff and Le Bel when they created stereochemistry.

These structural formulas are intended to picture the difference in the chemical and physical behavior of the various compounds by an arrangement which corresponds to the observed facts. The formula for acetic acid, which was long a subject of hot debate, provides an excellent example. In it, six parts by weight of carbon are combined with one part by weight of hydrogen and eight of oxygen. Precisely this same percentage composition is presented by such commonly known materials as formaldehyde, lactic acid, dextrose, and levulose. The molecular weight determination, which permits a sharp differentiation of many compounds having the same empirical formula, yields $C_2H_4O_2$ for acetic acid, a composition which likewise applies to glycolic aldehyde. An extended study of its properties was required to establish the simple formula for the acid. Obviously, its four hydrogens are not alike, because three of them can be replaced by other elements without the compound losing its acidic character (Dumas' chloro-acetic acids). If, however, the fourth hydrogen atom is replaced by any element whatsoever, the acid character is lost, and even when the three other hydrogen atoms are left untouched (sodium acetate, acetyl chloride). These findings indicate that the hydrogen atoms occupy different positions in the formula: CH_3-COOH. The entire behavior of acetic acid and its salts conforms to this method of representation. For instance, its electrolysis, which was first studied by Kolbe, yields hydrogen at the cathode and ethane and carbon dioxide at the anode. The observed volumes of H_2 and C_2H_6 are equal, whereas twice as much CO_2 is evolved as of either of the inflammable gases. Consequently, it seems logical to suppose that after the CH_3COO^- anions are discharged, they split in pairs to yield C_2H_6 and $2CO_2$.

Even though the formulas of organic chemistry developed quite differently from what had been in Berzelius' mind, nevertheless the shade of this great genius must have derived great satisfaction from the fact that his electrochemical theory was revived by his fellow countryman Arrhenius. Of course Berzelius would hardly be able to recognize his child, which had changed so much. The most important deviations from the laws of osmotic pressure, freezing and boiling point exhibited by aqueous solutions of salts, acids, and bases were explained by Arrhenius as due to a dissociation of the molecules into ions, and the resulting increase in the number of dissolved entities determines the irregularities, which hitherto had been inaccessible to mathematical examination. The ions, *i. e.*, oppositely charged atoms and radicals, correspond completely to the Liebig theory of acids. Since they are differentiated from the atoms and radicals by their charges, to which they owe their stability in solution, Wilhelm Ostwald proposed that the ions be provided with special signs to indicate the nature and number of units of charge carried by each. The dissociation theory again takes account of the dual nature of salts and connects them in more complete fashion with a host of otherwise inexplicable isolated facts.

The insight into the structure of the atom and the possibility of attacking the atomic nucleus have brought no fundamental changes into chemical symbolism. The atomic weight no longer determines the position of an element in the system; the characteristic determinant is the atomic number. The custom has now developed of placing the ordinal number below and the atomic weight (mass number) above the symbol of the element. Since Rutherford in 1909 produced hydrogen and a new isotope of oxygen by bombarding nitrogen with α-particles, *i. e.*, helium nuclei, the chemists have written such nuclear reactions in the form ${}_7N^{14} + {}_2He^4 \rightarrow {}_8O^{17} + {}_1H^1$. The atomic physicists abbreviate this to ${}_7{}^{14}N\ (\alpha, p)\ {}_8{}^{17}O$. In this expression, the first letter within the parentheses indicates the acting α-particle; the second letter, p, the proton liberated, while the symbols before and after the parentheses indicate the starting and end product, respectively.

Thus the chemical formulas are and remain the simplest conceivable expression of the composition of substances and the processes which occur between them. Their development from the ancient cabalistic signs, which at best served for labeling the glass and ceramic containers of the chemist's stock, was a gigantic feat of the human mind, which deserves proper appreciation from us moderns who use this convenient device, through which so much can be expressed by so little.

BLOOD-VOLUME DETERMINATIONS BY MEANS OF RADIOISOTOPE-LABELED RED CELLS

An Experiment in Biochemistry

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THE impact of the isotope on the theories and practice of medicine in the postwar years has been resounding. The tagged atom has led to drastic revision of previous concepts concerning biochemical dynamics, and has furnished often an inexpensive and accurate tool for the investigation of many physiological and analytical problems. It is imperative, therefore, that the training of medical students be amplified to include an elementary understanding of the techniques of isotopes and an appreciation of the potentialities of the new field.

The incorporation into the first-year biochemistry course of experiments in which tracers are used has posed numerous practical difficulties. Nucleonics and the theory of tracing and measurement of isotope dilution must be presented in a few elementary lectures. Problems of manipulation of radioactive materials, waste disposal, radiation hazards, contamination of working areas in limited space and facilities—all must be successfully handled. Fortunately, great simplification in experimental procedures is possible by a careful choice of isotopes with low levels of emitted energy and relatively short half-lives.

In this respect, the choice of radiophosphorus, P^{32}, is a judicious one, since the very minor contamination hazard and the relatively inexpensive equipment required make for optimum convenience. Ample proof of this is seen in the biochemical and medical literature where more than 500 articles dealing with this isotope have appeared, mostly in postwar years.

A laboratory procedure which has been determined to be most advantageous for first-year biochemistry students has been the determination of blood volumes by means of P^{32}-labeled red cells, following the simplified method of Kelly, *et al.*[2] This method has been modified herein for rabbits. Choice of this technique was planned and deliberate because of the numerous advantages it affords. In addition to the convenience of using radiophosphorus, the actual measurements, involving merely counts of diluted and undiluted blood, are very simple. The order of accuracy is reasonably high and the apparatus required—other than the Geiger tube and scaling instruments—is minimal and usually part of the inventory of a medical biochemistry laboratory. Since the method is in actual clinical practice in hospitals with available isotope facilities, the students are impressed by the opportunity to gain experience in an isotopic technique which has practical application. The safety factor considering the low levels of beta energy emitted by P^{32} is at least as high as that in handling the radioactivity emanating from watch or clock dials.

EXPERIMENTAL PROCEDURE

The determination of blood volume is accomplished by incubating blood cells from rabbits with 80 to 100 microcuries of P^{32}-labeled phosphate for 45 to 60 minutes at 37°C. Approximately 10 per cent of this activity is absorbed by the cells which are washed, reconstituted to volume with ACD buffer, resuspended, and injected into the animal. After an interval allowing for complete distribution of the labeled cells throughout the circulation, a blood sample is withdrawn for counting. The dilution of the activity of the cells (the volume of the whole blood) is obtained by dividing the activity of the injected cells by that of the blood withdrawn. Because of the greater instability of rabbit blood cells as compared to human blood cells, the procedure must include precautions usually not considered important in the handling of human blood. Hemolysis of rabbit erythrocytes is apt to occur if a proper suspending fluid (ACD) is not substituted for isotonic saline (NaCl), and if the cells are not agitated with caution and kept immersed in ice water. On the other hand, when dealing with rabbits it is not imperative but merely good practice to exercise aseptic handling of the instruments.

Equipment Necessary

ACD (acid-citrate-dextrose solution)—

Trisodium citrate	2.20% (w/v)
Citric acid	0.80%
Anhydrous dextrose	2.25%

It is advisable to make up the solution in 500-ml. lots and to keep it stoppered and refrigerated. Sterility is not necessary.

Ice-box centrifuge. If not available, cells may be spun in a regular centrifuge with care to immerse them in ice water as soon as they are removed from the machine.

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[2] KELLY, F. J., D. H. SIMONSEN, AND R. ELMAN, *J. Clin. Invest.*, **27**, 795 (1948).

Two 15-ml. centrifuge tubes, graduated in ml.
Wintrobe or Cutler tubes for hematocrit determinations
80 to 100 mc. P^{32}, as phosphate in dilute HCl
2 Tuberculin syringes, capacity 1 ml.
Two 24–26 gage $1^1/_2$-in. needles
2 Bulldog clamps
Planchets, 6 per experiment
Heparin
Parafilm, approximately one square foot
Four 1-ml. volumetric pipets
One 3-ml. blood pipet
Razor blades
Zylol or toluene, 10 to 20 ml.
Rabbit box or board
Duponal, 1 per cent solution, 5 to 10 ml.
2 Long-stem "nose" droppers
30-ml. syringe with 18 gage needle
Interval timer
Gauze
Silicone liquid for coating glassware to increase cell stability
4 Test tubes

Sterility is not necessary, but equipment should be chemically clean.

All glassware should be siliconed and dried. Silicone liquid is poured into all glassware, drained, and the glassware rinsed 3 to 4 times with water.

To all Cutler or similar tubes, a "pinch" of heparin (gage by tip of spatula) should be added.

Preparation of Tagged Cells. To two 15-ml. centrifuge tubes approximately 1.5 to 2 ml. of ACD are added.

A rabbit (in our experiments white rabbits are used) is prepared for cardiac puncture. Twenty to 30 ml. of blood is removed. Making sure the syringe has been wet with ACD solution, about 5 to 8 ml. blood is placed in one centrifuge tube and the balance is placed into the other. These are covered with parafilm and inverted 20 to 30 times to prevent clotting. Both tubes are placed in the incubator at 37°C. until ready for use, and inverted intermittently.

To the tube containing 5 to 8 ml. of blood are added 80 to 100 microcuries of P^{32} in a volume less than 1 ml. (to maintain isotonicity). The tubes are inverted 5 to 10 times and returned to the incubator for 45 to 60 minutes, inverting the tubes 10 times approximately every 5 minutes. Care is required to avoid shaking the tubes.

At the end of incubation time, the cells are spun down in an ice-box centrifuge at 2000 r. p. m. for 15 minutes. The supernate is removed with the aid of a nose dropper and replaced with cold ACD to the original volume. Recentrifuging and reconstituting to volume is repeated 3 times, mixing being done by careful inversion 20 to 25 times. In experiments where slight hemolysis is observed during the washing, it is advisable to eliminate the final one or two washings.

After removal of the third washing, the volume is replaced to the original with cold ACD. The tube is inverted gently 20 to 26 times or more and placed in the ice box until ready for use.

Preparation of the Tagged Cells for Counting Initial Activity. Since the tagged cells are too active to count conveniently, they are diluted serially with inert blood.

Into 4 small test tubes containing heparin are placed 3 ml. of blood. Care is required to prevent clotting. The pipet should be previously rinsed with ACD. To the first tube is carefully added, by means of a 1-ml. volumetric pipet, 1 ml. of the tagged red cells (making sure the cells are well mixed before the addition).

The tagged cells in the first tube have thus been diluted four times. One ml. of the 1:4 suspension in the first tube is now removed with a freshly rinsed (ACD) pipet and added to the second tube containing 3 ml. of untagged blood giving a 1:16 dilution (1:4 × 1:4). Transfers are continued until the fourth tube is prepared containing a 1:256 dilution of the initial milliliter of tagged cells. In each tube the activity is carefully mixed by drawing blood into and expelling from the pipet 15 to 20 times. A pair of 1-ml. portions of the activity in the final dilution is placed in planchet for counting. To each is added a drop of 1 per cent soap solution (duponal) to facilitate spreading in the planchet.

Injection of Radioactive Cells. The rabbit is weighed and placed in the box with a cover on tightly and so notched as to allow the head and ears to protrude. Both ears are shaved along the marginal ear veins.

The tagged cells are removed from the ice box and inverted to mix them well. One milliliter is carefully drawn into a tuberculin syringe and *all air bubbles* are removed. Holding the right ear *tightly*, the needle is introduced into the right marginal vein. Once in the vein, the needle is extended to the hilt. If the needle slides easily with little friction, the left thumb is placed over the needle and held *securely*, in order not to withdraw the needle if the animal moves its head. The cells are injected slowly and are infused readily if the needle is in the vein. The needle is then withdrawn and the site clamped with the Bulldog clamp.

After 20 minutes of equilibration in the rabbit, a sample is obtained for counting by making a nick in the left marginal ear vein. Zylol or toluene may be used on the surface of the ear to promote a more rapid flow. Several milliliters of blood are collected in a heparinized tube and 1 ml. is pipeted into a planchet. Five drops of duponal (about 1 per cent) are added.

The planchet of diluted tagged cells (1:256) and the one prepared from the animal are incubated at 37°C. to dryness (overnight). A third sample of untagged whole blood is similarly reserved to serve for taking background counts. For the sake of saving time the wet samples may be counted, but the counts are less reproducible and less accurate.

Plasma Volume. The plasma volume is found from the whole blood volume by doing a hematocrit determination and finding the plasma fraction of the whole blood volume. The tube with the remainder of the blood is spun at 2500 to 3000 r. p. m. for 60 minutes. The top level of the plasma at the meniscus is read. The level of the packed red cells is noted, ignoring the buffy coat. The second decimal is estimated in the reading.

Calculations. The instrument background is meas-

ured in counts per minute using a sample of inert blood. The experimental samples withdrawn from the animal are counted for a time interval corresponding to several thousand counts and the activity in counts per minute is recorded (E).

The activity of the injected sample (I) is found from the count of the diluted tagged blood (D) multiplied by the dilution factor (256), thus

$$I = D \times 256$$

The background count (B) is subtracted from both the experimental and injected samples. The whole blood volume (WBV) is therefore:

$$WBV = \frac{I - B}{E - B} = \frac{D \times 256 - B}{E - B}$$

These calculations are illustrated with the data from a typical experiment in the table.

Rabbit No. R2

Animal weight	3.20	kg.
Diluted tagged cells (D)	955.4	cts/min.
Experimental withdrawn samples (E)	1417	cts/min.
Background (sample of inert blood) (B)	24.16	cts/min.
Hematocrit (2600 r. p. m. for 45 min.)	42.35	%

$$WBV_{R2} = \frac{(955.4 - 24.16) \times 256}{(1417 - 24.16) \times 3.20} = 53.45 \text{ ml./kg.}$$

The red cell volume (RCV) is the WBV × blood fraction of cells (hematocrit):

$$RCV = 53.45 \times 0.4235 = 22.63 \text{ ml./kg.}$$

The plasma volume is then the whole blood volume minus the cell volume, thus:

$$PV = WBV - RCV = 53.45 - 22.63 = 30.82 \text{ ml./kg.}$$

A very useful trial recovery experiment based on the method of Reid and Orr[3] allows a preliminary trial in determining the volume of a unit of human bank blood (out-dated blood is very useful for this purpose) by injecting the suspended active cells into the bottle, gently agitating for one half hour, and then withdrawing from the bottle the samples to be counted. The bottle of bank blood serves as the experimental subject for the run. Various details are thus controlled and amply tested prior to any experimental run on a test animal. In detail, the control run is made as follows:

A 10-ml. volume of blood is withdrawn in a heparinized syringe from a bottle of bank blood. Six to 8 ml. of this are injected into a test tube containing 1 ml. of saline containing 50 to 100 ml. of P^{32}. The tube is agitated and then incubated at room temperature for ½ hour, after which spinning, drawing of plasma and supernates, and reconstituting of cells are performed as described. An accurately measured aliquot of the resuspended cells (1.00 ml.) is added to the original bottle of blood. After ½ hour of gentle mixing, two samples (2 ml.) are withdrawn for counting. The activities of these are compared with those of samples containing the same volume of the tagged original suspension. The latter, being too active to give accurate counts in the apparatus, are diluted 100 times with another sample of bank blood. The volume of the unit of bank blood is calculated and compared with the actual measured volume from:

$$WBV = \frac{\text{activity of diluted original cells}}{\text{activity of blood sample}} \times 100$$

Data obtained by students so far from three trial runs done in this manner show an accuracy of 2.1 per cent, with a total experiment time under 2 hours.

[3] Reid, A. F., and M. K. Orr, *J. Clin. Invest.*, **29**, 313–6 (1950).

DISCUSSION

The relative simplicity of the experiment allows for total working space on one 24 by 30-in table. This is covered with a large blotter so that any spilled active material may be readily discarded. The apparatus consists of a basic scaler and Geiger-Müller counter with a shielded manual sample changer. The counting apparatus is kept on a table separate from the working area. The errors in the procedure depend on the handling of the cell suspension, prevention of hemolysis, which occurs in rabbit blood much more readily than in human blood, and accurate measurements of the volumes of injected cells and the aliquot of radioactive diluted blood reserved for the count of initial activity. It has been our experience that larger values than those reported, 57.32, S.D. ± 4.82 ml./kg.,[4] are obtained when activity is lost in one of the following ways: (*a*) hemolysis of the cells results in the injection of cellular debris which is not equilibrated in the animal; (*b*) the injection of the 1 ml. of tagged blood into the marginal vein in a rabbit is a bit difficult for a beginning student and sometimes results in the deposition of the portion of the activity in the tissue surrounding the vein. This activity is not circulated in the blood and leads to a loss of counts (lower experimental activity). In general these factors leading to erroneously low counts in the experimental samples give high calculated blood volumes when divided into the counts per minute of injected activity.

The procedure employed makes use of whole blood for radiocounting, which is much simpler and more time-saving than preparing a cell suspension after distribution of the activity in the subject, and presumably also has an advantage in that the traces of activity which leak from the tagged cells into the plasma are counted. The radiation hazard is minimal to the animal or the experimentor, as is shown by Reid and Orr who give data for 110 humans with average uptake of the cells amounting to 7 per cent of the 100 microcuries incubated, with the largest single uptake of 19.5 per cent. In calculating the hazard when the activity was injected into a human, these authors assumed a 20 per cent uptake. In a 50-kg. individual this would calculate to 0.07 rep. for approximately one week, which would diminish to 0.035 rep. in 2 weeks (14.3 days half-life). This calculated value is deliberately high as it assumes no excretion but is yet a small fraction of the normally permissible 0.5 rep. Therefore,

[4] Armin, J., R. T. Grant, H. Pels, and E. B. Reeve, *J. Physiol.*, **116**, 59–73 (1952).

no radiation hazard is encountered if but minor attention is paid to precautions. Indeed, it is our opinion that the students are exposed to greater dangers in their other experiments by handling corrosive acids and hot solutions. The most painstaking detail in the measurement of blood volumes is the required aseptic handling of syringes, tubes, and needles in withdrawal and injection of the cells, which for animals is not required but is definitely good practice. In addition, as a means of illustrating fully the manner of working with isotopes, the students are required to characterize the radiophosphorus they use in calibrating its millicurie strength against a set of simulated reference standards. They are also required to count a sample daily for 2 minutes, for seven or more successive days, in order to calculate the half life of the P^{32} used, and thus to identify it. This also affords a check on the purity of the isotope shipment, and acquaints the student with the main remaining features of low energy isotope experimentation.

The data taken by means of tagged cells may be independently checked by means of the more conventional dye techniques although the correlation is not exact. The chief advantage of the tagged cell method is that it measures directly the total cellular volume, whereas the dye-dilution techniques provide a means for obtaining the plasma volumes directly. Measurement of whole-blood volume by either method depends on the blood hematocrit (the ratio of cells to plasma). The hematocrit of blood drawn from a large vessel may or may not be a true indication of the general body ratio (for instance as in capillaries) of cells to plasma. Hence the whole-blood volumes obtained by the dye and tagged-cell methods do not exactly check. The values for whole-blood volumes obtained by tagged-cell techniques approximate 10 per cent greater than those obtained by Evans dye, and the exact amount of difference is as yet controversial. For these reasons the simultaneous combination of both methods, although promising, has not been incorporated into the experiment described. Also, in our opinion, it would constitute a task too formidable and time-consuming for students. Although the experiment as described here, when condensed into a laboratory work-week of about 11 hours, demands the full attention of the instructor and requires his close supervision, the benefits to the student are numerous, his interest is compelled by the "magic" of the word *isotope*, and the effort bears definite reward for the energy expended.

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THE great advances in qualitative analysis during the past several decades are due in large part to the introduction of many new reagents, most of them organic. The ordinary working chemist has neither the time nor materials to determine which of these important aids have the special characteristics that fit them for a particular analytical problem, nor does he usually have access to the widespread literature in which the suggested reagents are described. Consequently, the Union Internationale de Chimie recognized a real need when, at its Madrid (1934) meeting, it set up an "International Committee on New Analytical Reactions and Reagents." Its assignment was to prepare and publish, at suitable intervals, critical reports on new analytical reactions. The first report was issued at Leipzig in 1938 as "Table of Reagents for Inorganic Analysis."[1] It covered the period 1910–36 and because of the large number of compounds that needed to be considered it was comprehensive rather than critical and selective. The tables were constructed from the literature and the recommendations regarding the serviceability of the new reagents were mainly based on the claims of the discoverers. The volume was well received and further issues were hopefully anticipated.

It was planned to publish the reports at 2- or 3-year intervals and to make them more objective by having the new reagents tested by the committee or its representatives. It was decided to add ten correspondents to the committee to collaborate in the experimental work. However, the advent of World War II made it impossible for the committee to keep in touch with each other; the project was threatened with abandonment, but the importance of the idea kept it alive. The original committee[2] was dissolved in 1940 and a commission of three appointed to continue the work. They were: van Nieuwenburg, J. Gillis (Ghent) and P. E. Wenger (Geneva). Despite obvious handicaps, they set out to study the new reagents that had been de-

[1] This tabular summary, in French, English and German, (409 pages) was reprinted at Ann Arbor in 1944 by authority of The Alien Property Custodian.

[2] W. Böttger (Leipzig); F. Feigl (Vienna); A. S. Komarowsky (Odessa); N. Strafford (Manchester); C. J. van Nieuwenburg (Delft) Chairman.

scribed since the compilation of the first report and also some that had been included there. The second report was published at Basle in 1945. The reagents had been carefully screened, and not more than five were recommended for any one element, in most cases less than five. The pertinent data regarding the selectivity, sensitivity, etc., of the chosen reagents were determined or checked. Most of this experimental work was done in Wenger's laboratory by his associate R. Ducket, who also assisted him in the editorial work. Therefore, this second report[3] is essentially their product.

The third report[4] appeared in 1948. It was issued by van Nieuwenburg and Wenger as President and Secretary, respectively, of the Commission. In form it was identical with the first report. The compilation was made by Clément Duval, who was now a member of the commission. The years covered were 1937–47.

The fourth (and latest) report was published in Paris in 1950.[5] It is the successor to the second report and covers the period 1943–47. Like its predecessor, it deals with a series of carefully selected reagents in a critical fashion. The data were secured by a rather large number of collaborators,[6] but again the volume was mainly a product of Wenger's laboratory and editorial desk. His chief assistant in this case was Mlle. Y. Rusconi.

Paul Eugéne Etienne Wenger was born at Geneva on April 27, 1888. All of his training and professional career have been centered in his native city. He entered the University of Geneva in 1906, the *docteur ès sciences physiques* was conferred in 1911. The thesis, prepared under the guidance of L. Duparc (1866–1932) dealt with the solubility of magnesium ammonium phosphates and arsenates. Dr. Wenger was assistant in analytical chemistry from 1910 to 1912; he habilitated as Privatdozent in 1912; he was made Directeur des Thèses et Travaux des Recherches in 1914. He was advanced to Professeur Extraordinaire in 1918 and in 1933 was appointed Professeur Ordinaire de Chimie Analytique in the Faculty of Sciences and Directeur de l'Institut de Chimie Analytique et de Microchimie. Since 1946 he has served as Dean of the Faculty of Sciences.

At the beginning of his independent career he and his collaborators confined their research activities to pure and inorganic analytical chemistry. They especially studied new methods of detection and determination, new separations, etc. For several years they worked on the catalytic production of ammonia and eventually found a catalyst that functions at a much lower temperature and pressure than foreseen in the Claude or Haber process.

His interests took a new turn in 1930: a laboratory for microanalysis with all the latest equipment was set up. It has been extremely active and many studies dealing with the direct applications of this methodology to analytical problems and also to biological questions have been carried to a successful conclusion there. Parallel to these investigations, he and his students dealt extensively with organic reagents as regards their use first in microanalysis and then in macro procedures. His studies of the selection of reagents for qualitative inorganic purposes led, as we have seen, to a major contribution to the international reports on reagents and reactions. These studies also led him to the development of a new semiquantitative method for the rapid determination of small amounts of certain metals. In brief, the solution of the sample is diluted progressively according to a systematic scheme until it no longer gives a positive spot test with the chosen reagent. Comparison with a table constructed from the results obtained with a standard solution gives the necessary data for the calculation of the amount of metal, *e. g.*, copper, present.

A laboratory for instrumental work has recently been installed. His studies of reagents are now being extended through applications of the results delivered by polarography, potentiometry, colorimetry, and spectrography. These added approaches make it possible to secure much more fundamental information about certain reagents and their behavior under particular conditions.

More than 150 papers have come from his laboratory. In addition to the reports discussed above, he has also published: (with G. Gutzeit) "Manuel de chimie analytique qualitative minérale" (496 pp.) (1934); (with R. Duckert and Y. Rusconi) "Traité de chimie analytique qualitative minérale" (466 pp.) (1946); (with D. Monnier and Y. Rusconi) "Manuel théorique et pratique d'analyse chimiques qualitative et volumetrique" (188 pp.) (1948).

Professor Wenger has been a member of the editorial board of *Mikrochimica Acta* and *Mikrochemie* since 1937. When the war caused many of the analytical journals to go under entirely or temporarily, he helped to fill the gap by founding *Analytica Chimica Acta*. He has been its chief editor since 1946.

Well known in scientific circles, he is constantly in demand for lectures and courses. He has served in this capacity in France, Belgium, Holland, Jugoslavia, Austria, and Brazil.

He holds many medals and honorary memberships. He is vice-president of the Analytical Section of the International Union of Pure and Applied Chemistry; President of the Scientific Section of the Swiss National Committee for UNESCO; member of the Conseil de la Chimie Suisse, etc. In short, he is a very active and useful member of the scientific community of nations.

[3] "Réactifs pour L'Analyse Qualitative Minérale; Deuxieme Rapport de la Commission Internationale des Réactions et Réactifs." (288 pages).—The essence of this report is also available in "Reagents for Qualitative Inorganic Analysis" by C. J. van Nieuwenburg and J. Gillis (379 pages) New York, 1948. This is not a literal translation.—For a history of the project through the second report see VAN NIEUWENBURG, C. J., *Bull. soc. chim. France*, 1946, 188–192; WENGER, P. E., *ibid.* 193–197.

[4] "Tableaux des Réactifs pour L'Analyse Minérale," Paris (201 pages). It was also published in New York (1949) with the title "Table of Reagents for Inorganic Analysis."

[5] "Réactifs pour L'Analyse Qualitative Minérale" (104 pages).

[6] G. Charlot, D. Bezier, C. Duval, J. Gillis, J. Hoste, J. Matthews, C. J. van Nieuwenburg, A. Ocak, N. Strafford, J. H. Yoe in addition to the principal authors.

THE KINETIC STRUCTURE OF GASES[1]

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In an effort to portray a working model for the kinetic structure of gases, a mechanical system was developed which exhibited a distribution of displacements which was in outward respects similar to the Maxwellian distribution relationships. A quantitative analysis of the model by means of photography revealed a surprising agreement with the classical distribution of velocities. This analysis not only provides a directly visible analogy to the gaseous structure, but offers a classroom demonstration of the distribution character of the linear displacements of gaseous molecules.

The model, which involves an extension of that of Woolley and McLachlan,[2] was constructed of parallel glass sides 1 cm. apart and 15 cm. square, mounted in a wooden frame. This glass-enclosed volume contained approximately 200 2-mm. glass beads. Glass beads were found to be superior to metal because of their high degree of elasticity in collisions. Figure 1 shows the

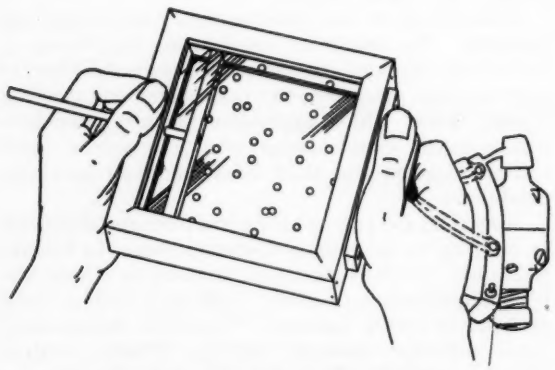

Figure 1. Apparatus for the Demonstration

details of the model, which includes a piston that is controlled at one side of the box. On the opposite side of the box a rigid extension was provided which served as a handle. In operation, this handle is supported by one hand to which is fastened a massaging vibrator such as is commonly available on the market at present. The other side of the box is supported by the other hand so that the box may be held horizontally at a distance of 3 or 4 cm. above the field of a vertical or overhead projector.[3] The image which is projected on the screen consists of circular shadows of the beads, each exhibiting a bright center. The motions of the beads are primarily in the horizontal plane, where the beads collide rapidly with each other and with the walls of the container. These collisions appear to be elastic and as a result depict in a very effective manner the kinetic structure of gases.

This model may be used to demonstrate the effect of temperature on a gas by increasing or decreasing the amplitude of vibrations which is simply controlled by the grip of the hands. The tighter the box is held by both hands the greater the amplitude of the vibrations transmitted to the box. Energy imparted by the vibrating walls of the box to the glass beads results in translational motion of the glass beads which is uniformly random and at an apparent mean velocity which is proportional to the tension with which the box is held.

Upon moving the piston and confining the beads to a smaller volume, the translational motions of the beads become greatly increased. This phenomenon parallels in an excellent fashion an adiabatic compression of a gas, wherein the resultant increase in pressure is accompanied by an increase in temperature.

Change of state can be dramatically shown by slightly tilting the box so that the beads roll to one side of the box. Slight vibration causes the spherical beads to find their positions in the closest-packed cubic structure of a solid. A small amplitude of vibration supplied by the mechanical vibrator causes the beads to oscillate about their lattice positions, whereas larger vibrational energy produces displacements great enough to destroy the lattice formation. The resulting structure is that of a liquid. A further increase of vibrational energy produces an occasional "hot" molecule which breaks away from its neighbors and evaporates, a situation shown in Figure 2. Finally, by increasing the amplitude of vibration and returning the box to a horizontal position, the liquid becomes completely transformed to a gas.

The velocity distribution of the glass beads was analyzed by photographing the projected image of the box on a screen. Figure 3 is a photograph of this type made at 1/50 second exposure. The velocities of the beads were determined by measuring the length of the blurs of the beads on the photographic image. Measurements were based upon 10 units as the diameter of the bead.

In the photographic analysis of this model the amplitude of vibration was varied between the lowest degree of vibration which produced uniform distribution of motion and the maximum degree of vibration. This gave a series of photographs from which the velocity distribution data were collected. Two of these curves are plotted in Figure 4. The observations are shown

[1] Presented at the 122nd Meeting of the American Chemical Society, Atlantic City, September, 1952.

[2] Woolley, Roscoe H., and Dan McLachlan, J. Chem. Educ., **27**, 187 (1950).

[3] Slabaugh, W. H., J. Chem. Educ., **28**, 579 (1951).

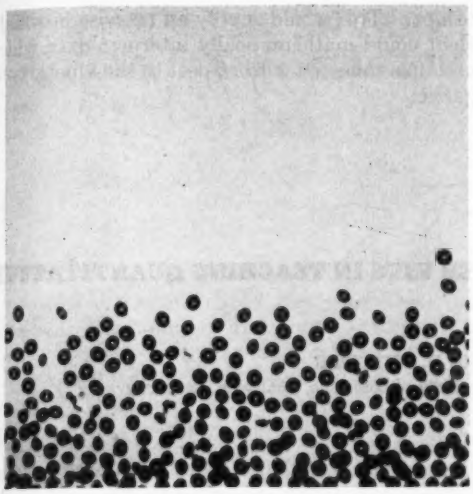

Figure 2. The Process of Evaporation from a Liquid

as points and the solid curves represent the distribution of velocities calculated from the Maxwell equation for the distribution of velocities in the $x + dx$ direction. That is,

$$N_{dx} = \frac{4N}{\alpha\sqrt{\pi}} \cdot \frac{x^2}{\alpha^2} \cdot e^{-\frac{x^2}{\alpha^2}} dx$$

N_{dx} is the number of molecules with velocities between x and $x + dx$, N is the total number of molecules in the system, α is the most probable velocity, and x is the velocity of a given molecule. The two curves in Figure 4 represent the velocity distributions for systems wherein the most probable velocities (the maximum in the curves) are 4 and 5 units, respectively.

It is to be noted that the agreement between the observed and the calculated values is good. As the temperature (amplitude of vibration) is increased the distribution curve broadens and the number of molecules with the most probable velocity decreases. It is predicted that a larger number of beads would give better agreement because of the statistical nature of the theory upon which the Maxwell law is established.

A comparison of the distribution curves obtained from several different temperatures (amplitudes of vibration) points toward a verification of the Arrhenius equation for the energy of activation. A modified form of this equation is where N' is the number of

$$\frac{N'}{N} = e^{-\frac{E}{RT}}$$

activated molecules, N the total number of molecules, E the activation energy, and T the temperature. Since it was not possible to quantitatively observe the temperature (amplitude of vibration), except to note the most probable velocity which was based upon arbitrary units, the verification of the Arrhenius equation could be made only qualitatively. In the following table the ratios N'/N are compared to the most probable velocity

Most probable velocity (α)	$\frac{N'}{N}$
4	0.005
5	0.05
6	0.11
8	0.35

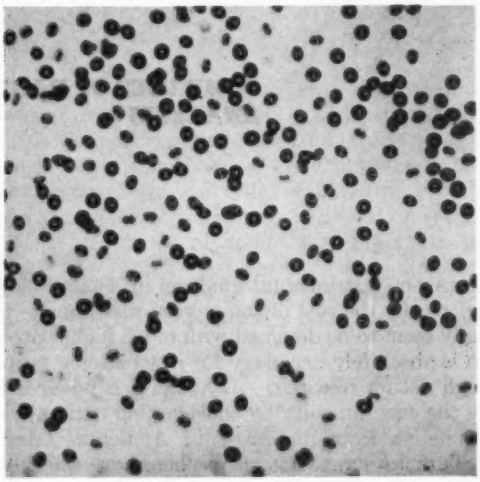

Figure 3. Beads in Motion Photographed at $^1/_{50}$ Second

for four of the systems observed. An arbitrary value of $E = 11.5$ on Figure 4 was selected as the activation energy. The fundamental concept that a 10° rise in temperature doubles the reaction rate, the reaction rate being primarily dependent upon the number of activated molecules, is substantiated.

This model not only provides for the lower-level courses a simple and direct demonstration of some of the fundamentals of gas structure but it is readily adaptable to upper levels of instruction in the topic of

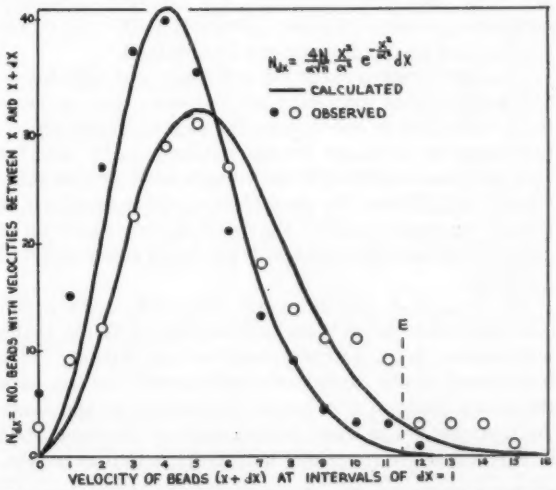
$N_{dx} = \frac{4N}{\alpha\sqrt{\pi}} \frac{x^2}{\alpha^2} e^{-\frac{x^2}{\alpha^2}} dx$
CALCULATED
OBSERVED
E
N_{dx} = NO. BEADS WITH VELOCITIES BETWEEN x AND x+dx
VELOCITY OF BEADS (x+dx) AT INTERVALS OF dx = 1

Figure 4. Velocity Distribution for Two Observed and Calculated Systems

kinetic theory. It is suggested that in these latter courses photographs of this model, such as Figure 3, would provide the necessary information with which to validate the velocity distribution and activation energy relationships. This would supply an exercise in which the student could mathematically interpret data which he himself has collected with respect to the kinetic concept of gases.

SOME USES OF RADIO SERVICE KITS IN TEACHING QUANTITATIVE ANALYSIS

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THE use of instrumental analysis in small colleges is restricted by the cost of commercial instruments which usually seem to be designed with much higher precision than is absolutely necessary for instructional purposes, though not for research. Although it is possible to relieve the cost difficulty by constructing titrimeters and colorimeters from directions in *Analytical Chemistry* and THIS JOURNAL, not all teachers have the skill and experience in electronics, especially when using directions often scantily detailed, to produce attractive constructions. No matter how well the instrument functions, students are not likely to consider it a professional tool unless it has a professional appearance.

The problem of obtaining inexpensive and practical instruments to supplement conventional equipment specifically designed for chemical purposes has been partially solved in our quantitative analysis course by the purchase of radio service instrument kits, which can be put together without previous training in electronics simply by following the detailed assembly instructions. Such kits are available from several manufacturers at low cost. For less than $125, for example, a battery eliminator, a vacuum-tube voltmeter, a 400-volt power supply, and an oscilloscope can be obtained.[1]

The battery-eliminator kit was easily put together in one hour. This unit supplies voltages varying from 0–15 volts and is convenient for electrodeposition experiments or to charge storage batteries to be used for this purpose. Although the voltage may not be sufficiently well filtered for close electrolytic separations, it is more than adequate for the usual electrodeposition of copper in brass when used with platinum electrodes and a stirrer.

An a.-c., d.-c. vacuum-tube voltmeter, with a full scale deflection of 1.5 volts on its minimum range, is the next easiest of the four instruments to construct. This instrument is not completely satisfactory for use as a titrimeter because it is not very sensitive to the small voltage changes of most potentiometric titrations, but it is suitable for titrations with large potential breaks, for example the reaction of ferrous ion with ceric salts.

A power-supply kit giving up to 400 volts of direct current is useful as the supply voltage for vacuum phototubes in homemade colorimeter designs. It is practical to connect the phototube in series with a high resistance (1–20 megohms), the power supply, and a galvanometer or microammeter. The electrical circuit of a one-cell colorimeter thus obtained is as useful as the more common barrier-layer cell colorimeters and is more versatile, since different types of phototubes (such as the RCA 917, 926, and 929) functioning in different portions of the spectrum may be used.

An oscilloscope is the most complex of these instruments. It is used in our laboratory as balance detector in an a-c. Wheatstone bridge circuit for conductometric titrations. Although some may question the replacement of a $2 pair of ear phones with a $45 oscilloscope, the advantage of visual over aural operation is a real one. The well-known uses of oscilloscopes for other purposes[2] make this a very desirable instrument.

In addition to these four instruments, inexpensive decade resistance, decade condenser, and resistance substitution kits have proved useful as components in student Wheatstone bridge, potentiometer, and other circuits. The accuracy of these kits is not high (of the order of 1 per cent) by research standards but is sufficient for student experiments. Potential uses in chemistry for such other kits as an audio oscillator, grid dip meter, and impedance bridge are easily seen but will not be discussed here.

These radio service kits are excellent as an introduction to the construction of more difficult circuits described in the chemical literature. The variety introduced into a course in quantitative analysis by the use of these instruments is very helpful in dispelling the frequent impression that analysis consists of the monotonous manipulation of balance and buret. In modern chemistry analysis actually offers a greater variety of methods than any other branch of chemistry, and it is good to convince the student of this as early as possible.

[1] Most of the kits here described were purchased from the Heath Company of Benton Harbor, Michigan.

[2] RUITER, J. H., "Modern Oscilloscopes and Their Uses," Murray Hill Books, New York, 1949.

THE ENTROPY CHANGES ACCOMPANYING ASSOCIATION REACTIONS IN SOLUTION[1]

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THE extent to which a reaction will proceed at a given temperature is determined by the concentration conditions and the standard free-energy change accompanying the reaction at that temperature. The standard free-energy change is related to the changes of other thermodynamic quantities, the enthalpy and entropy, by the equation:

$$\Delta F^0 = \Delta H^0 - T\Delta S^0$$

For the purpose of gaining an insight into the factors which cause reactions to take place, it is worth while to consider the free-energy change to be a consequence of the corresponding enthalpy and entropy changes. The enthalpy change is related to the difference of the bond energies of the products and reactants, and in the case of reactions occurring in liquid media, to the difference of solvation energies of the products and reactants. The entropy change, on the other hand, is related to the change in randomness in the system which accompanies the reaction. An increase in the entropy of a system corresponds to an increase in the randomness of that system; the greater is this increase in randomness which accompanies a reaction, the greater is the extent to which the reaction will go. This influence which the entropy change of a reaction has in determining the free-energy change is shown by considering the two reactions:

H_2O (liquid, 25°C.) = H_2O (solid, 25°C.)
H_2O (liquid, 25°C.) = H_2O (gas, P = 1 cm. Hg, 25°C.)

The first of these reactions is not spontaneous, although it is exothermic ($\Delta H = -1650$ cal.), for it has an entropy change of -6 cal. mol^{-1} degree^{-1}. Water molecules have more freedom in the liquid state than in the solid state; the negative value of the entropy change is just as expected. The second reaction does go in spite of its extremely endothermic character; the value of ΔH is +10,500 cal. A large increase in entropy accompanies the reaction ($\Delta S = +41.5$ cal. mol^{-1} degree^{-1}). This large entropy increase reflects the much greater randomness of the water molecules in the gaseous state than in the liquid state. Corresponding reactions for the solidification of any liquid at a temperature above the melting point or for the vaporization of the liquid to give vapor at a pressure below the saturation pressure would equally well illustrate the importance of the entropy change in determining the free-energy change of a reaction. Thus, it may be said that there are endothermic reactions which go because of favorable entropy changes, and exothermic reactions which don't go because of unfavorable entropy changes.

Because the entropy change for a reaction is a measure of the change in randomness within the reaction system, it is expected that association reactions occurring in the gas phase will be accompanied by a decrease in entropy. This expectation is realized; typical data are given in Table 1.

TABLE 1
Entropy Changes in Association Reactions Occurring in Gas Phase

Reaction	ΔS(*e. u.*)	*Temp.*	*Ref.*
$2NO_2 \rightleftarrows N_2O_4$	−42.2	25°	(*1*)
$2I \rightleftarrows I_2$	−24.1	25°	(*1*)
$NH_3 + (CH_3)_3B \rightleftarrows (CH_3)_3BNH_3$	−39.9	100°	(*2*)
$N(CH_3)_3 + (CH_3)_3B \rightleftarrows (CH_3)_3BN(CH_3)_3$	−45.7	100°	(*2*)

Mere examination of the conventional equations for the reactions of association of ions in solution, equations which show a net decrease in the number of particles accompanying reaction, might lead to the expectation that the entropy change in such reactions would also be negative. This expectation is not realized. The entropy change in the reaction of hydrogen ion with the anion of a weak acid is always positive and an increase in entropy accompanies the formation of many complex ions from the constituent positive and negative ions. This apparently anomalous character of association reactions in solution is more easily understood after an examination has been made of the entropies of ions and molecules in solution.

ENTROPIES OF DISSOLVED SUBSTANCES

A definite relationship is observed between the entropy of an ion in aqueous solution and its charge, radius, and mass. R. E. Powell and W. M. Latimer (*3*) have shown that the standard partial molal entropy, S°, of a very large number of monatomic ions is given very closely by the equation:

$$S^\circ = (3/2)R \ln M + 37 - 270\, Z/r_e^2 \qquad (1)$$

where M is the atomic weight, Z is the absolute value of the charge on the ion, and r_e is the effective ionic radius. The value of r_e was taken to be 2.00 Å greater than the crystal radius for cations and 1.00 Å greater than the crystal radius for anions. These authors used the crys-

[1] Based in part on a talk presented before a Symposium on Equilibrium and Rate Behavior of Complex Ions held at the University of Chicago, February 21–23, 1951. This symposium was sponsored by the Office of Naval Research and the Atomic Energy Commission.

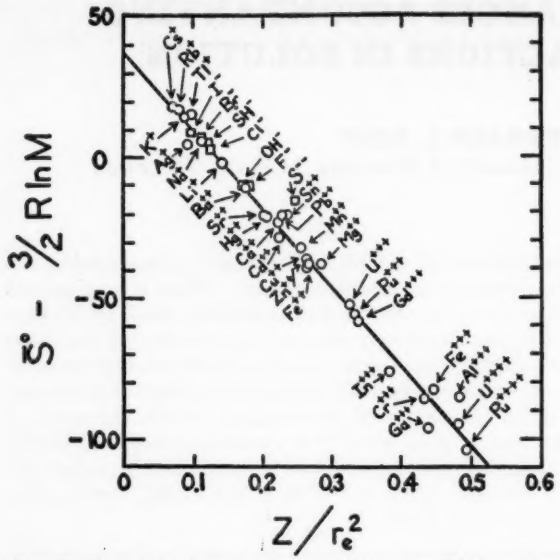

Figure 1. Corrected entropy in aqueous solution versus Z/r^2 for various ions.

(Figure through the courtesy of R. E. Powell and W. M. Latimer and with the permission of the editor of the *Journal of Chemical Physics.*)

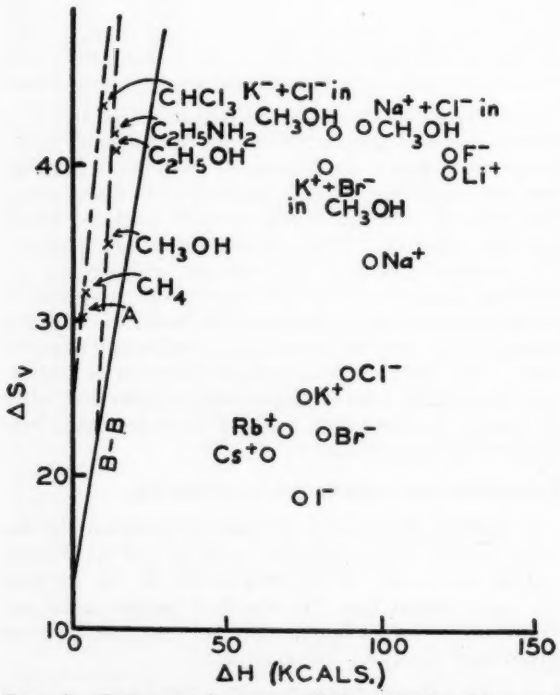

Figure 2. ΔS of vaporization versus ΔH of vaporization of ionic and non-ionic solutes from water (and from methyl alcohol in the indicated cases).

The solid line is the Barclay-Butler line. The values of the ΔS_v are 8 e.u. more positive than the ΔS_v based on the standard states discussed here (i.e., one molal solution, one atm. pressure).

(Figure through the courtesy of H. S. Frank and M. W. Evans and with the permission of the editor of the *Journal of Chemical Physics.*)

tal radii which are given by Pauling (*4*). The agreement between the experimentally determined values of S° and those calculated using equation (1) is shown in Figure 1 which has been reproduced from the paper by Powell and Latimer. Over a very wide variation of the quantities involved, the agreement between the observed and calculated values of S° is quite good.[2] The large loss of entropy which accompanies the solution of a gaseous ion, particularly an ion of high charge, is due primarily to the great loss of freedom which the water molecules suffer in becoming coordinated with an ion.[3] A part of this decrease in entropy is, of course, a consequence of the loss of freedom of the gaseous ion upon entering the condensed phase.

It must be pointed out that the entropies of solution of gaseous ions are more positive than might be expected in view of the large values of the heat of solution of gaseous ions. The basis of this expectation is the Barclay and Butler empirical rule concerning the ΔH and ΔS of vaporization (*6*). These authors have plotted the ΔS of vaporization versus the ΔH of vaporization at 25°C. for (*a*) gases from various nonassociated solvents, (*b*) carbon disulfide, chloroform, benzene, and chlorobenzene from acetone, (*c*) the four lower alcohols from benzene, and (*d*) a number of nonassociated liquids as pure substances. All of the points fall close to a straight line corresponding to the equation: $\Delta S_v = +14.5 + 0.0011\ \Delta H_v$ (the units are cal. mol^{-1} for ΔH, and cal. mol^{-1} degree $^{-1}$ for ΔS; the standard states are 1 atmosphere for the gas, and the pure liquid for the solutes). A graph which shows the ΔS and ΔH of vaporization from solution for some ions, as well as neutral molecules, is presented as Figure 2. It is clear that the gain of entropy of the system upon transferring an ion from the solution to the vapor phase is much smaller than would be predicted on the basis of the Barclay and Butler relationship. This conclusion that an ionic solution has "too much entropy" is explained by H. S. Frank and M. W. Evans (*7*) by picturing a region outside of the first coordination sphere in which the water structure is more broken down than it is in ordinary liquid water.

It becomes evident that factors other than ionic charge have an important bearing on the entropy of solution of gaseous species in water when one compares the entropy changes associated with two reactions which involve isoelectronic substances:

$$K^+(gas) + Cl^-(gas) = K^+(aq.) + Cl^-(aq.)$$
$$2A(gas) = 2A(aq.)$$

The values of ΔS° are -36 and -44 e. u. respectively,

[2] The entropy values plotted in Figure 1 are conventional ionic entropies. They are based upon $\bar{S}^\circ = 0$ for hydrogen ion. Since the true ionic entropy of hydrogen ion is close to zero (*5*), these values may be considered as true ionic entropies. (The error caused by this assumption is proportional to the charge on the ion. This follows from the fact that the directly measurable quantities are the sums of the entropies of equivalent amounts of positive and negative ions and the differences of the entropies of equivalent amounts of ions of charge of the same sign.)

[3] The values plotted as the ordinate in Figure 1 are equal to the entropies of solution of the gaseous ions plus 26.00 e. u.

if the standard states are one atmosphere pressure for the gas and the hypothetical molal solution for the dissolved substances. It is seen that the presence of the charges actually decreases the amount of entropy lost in the reaction.[4] Solution of a nonionic solute in water is generally accompanied by a decrease in entropy. The values of $\Delta S°$ of solution for a number of nonionic solutes in water are plotted versus the molal volume of the solute in the pure liquid state in Figure 3. This straight line relationship was observed by Powell and Latimer (*3*), from whose paper this figure is reproduced. In contrast to the case of ionic substances, the $\Delta S°$ of solution of nonionic solutes in water is more negative than would be expected on the basis of the Barclay and Butler relationship (*6*) in view of the low values of the ΔH of solution. This is shown in Figure 2. It appears that the water molecules lose considerable freedom when a nonionic solute is dissolved in water; the entropy decrease is very much greater than could be accounted for by the loss of freedom of the solute molecules. Frank and Evans (*7*) picture the nonpolar solute causing the "freezing" of solvent water molecules in the vicinity of the solute molecules. As the temperature is raised, these regions of "frozen water" melt, giving rise in the case of the noble gases to enormous partial molal heat capacities, which may exceed 60 cal. mol^{-1} degree.$^{-1}$ The correlation of $\Delta S°$ of solution with the molal volume of the solute is not inconsistent with this picture because larger molecules would bring about more "freezing of water" than would smaller ones.

Since we wish to consider the entropy changes associated with the formation of complex species which may be ionic, it is desirable to examine the entropies of some polyatomic ions in aqueous solution. The entropies of many such ions are more negative than would be expected from consideration of the net charge and size alone. The entropies of UO_2^+, UO_2^{++}, Cs^+, and Ba^{++} are presented in Table 2. The factors of size and mass

TABLE 2

A Comparison of the Entropy of Monatomic and Polyatomic Ions of the Same Charge

Charge		$S°_{298°}$		$S°_{298°}$
+1	UO_2^+	12 (*8*)	Cs^+	31.8 (*8*)
+2	UO_2^{++}	−17 (*9*)	Ba^{++}	3.0 (*8*)

would lead to the expectation that the entropies of the polyatomic uranium ions would be more positive than the entropies of the simple ions. The opposite is observed. In these nonspherically symmetrical ions, the solvent is not completely shielded from the higher charge on the central ion; certainly the charges on the uranium atoms of oxidation number +5 and +6 are greater than +1 and +2. If one assumes that the uranium atom and oxygen atoms are bonded by a single bond, the formal charges on the uranium atoms are +3 and +4. It is really not surprising, therefore, to find the entropies of these uranium ions more negative than the entropies of simple ions of the same net charge.

The entropies of some closely related polyatomic ions are presented in Table 3. It is seen that the entropy is

TABLE 3

The Entropies of Structurally Similar Polyatomic Ions in Aqueous Solution at 25°C.

Charge	P^V		S^{VI}		Cl^{VII}	
−1	$H_2PO_4^-$	21.6 (*10*)	HSO_4^-	30.6 (*11*)	ClO_4^-	43.6 (*11*)
−2	$HPO_4^=$	−8.7 (*10*)	$SO_4^=$	4.4 (*11*)		
−3	$PO_4^{\equiv}$	−52 (*10*)				

not determined exclusively by the size and net charge of the ion. There are large differences between the entropies of the ions which have the same charge, even though the sizes of these ions must be very nearly the same. The data for the three phosphate ions and the series of ions: perchlorate, sulfate, and phosphate ion indicate that the dependence of the entropy upon charge is greater than first power. This trend is important in determining the relative acid and base strengths and, presumably, the complex forming tendencies of these species.

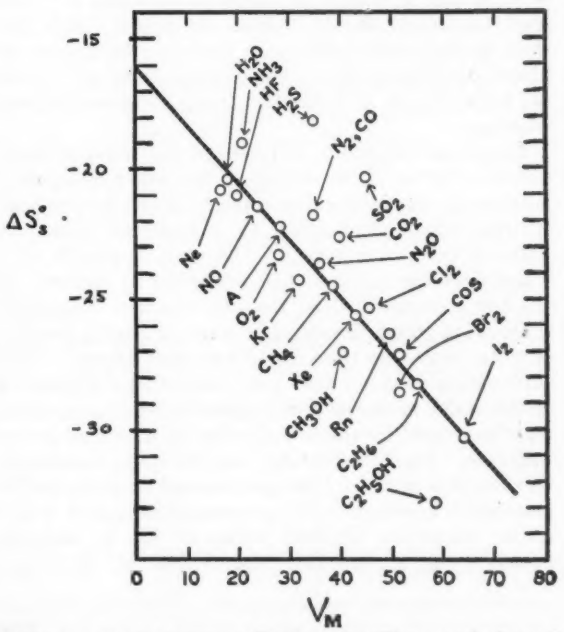

Figure 3. $\Delta S°$ for the process: X(g, 1 atm.) → X(aq., standard state 1 molal solution) versus the molal volume of the solute as the pure liquid.

(Figure through the courtesy of R. E. Powell and W. M. Latimer and with permission of the editor of the *Journal of Chemical Physics*.)

The factors which determine the entropy of a substance in aqueous solution are not simple. Certain trends have been observed, however, and these will be of value in our discussion of the entropy changes which accompany association reactions in solution.

[4] This comparison was pointed out by Frank and Evans (*7*).

TABLE 4

Reaction	*Temp.*	$K \times 10^{-10}$	ΔH(kg.-cal.)	$\Delta S°$(e. u.)	*Ref.*
$H^+ + NH_3 = NH_4^+$	25°	0.164	−12.4	+ 0.5	(12)
$H^+ + MeNH_2 = MeNH_3^+$	25°	4.16	−13.09	+ 4.7	(12)
$H^+ + Me_2NH = Me_2NH_2^+$	25°	6.21	−11.88	+ 9.5	(12)
$H^+ + Me_3N = Me_3NH^+$	25°	0.65	− 8.83	+15.3	(12)
$H^+ + EtNH_2 = EtNH_3^+$	30°	2.84	−13.58	+ 3.1	(13)
$H^+ + Et_2NH = Et_2NH_2^+$	30°	6.32	−12.77	+ 7.2	(13)

REACTIONS OF AN ION AND A MOLECULE

The entropy changes for reactions in solution between an ion and a neutral molecule to form a polyatomic ion show wide variations. It does not appear that any simple theory explains the observed trends. It is worth while, nevertheless, to examine some of the existing data.

A reaction of this type which has been rather well studied is the reaction of hydrogen ion with an amine to give an ammonium ion:

$$H^+(aq.) + NR_1R_2R_3(aq.) = \overset{+}{H}NR_1R_2R_3(aq.)$$

where R_1 may be a hydrogen atom or an alkyl group. The effect of successively replacing the hydrogen atoms of ammonia by methyl or ethyl groups is shown by the data in Table 4. It is seen that all of the $\Delta S°$ values are positive and that they become more positive as hydrogen atoms are replaced by alkyl groups. The change of the $\Delta S°$ value per substitution of a methyl group is approximately constant.

Evans and Hamann (*13*) discuss the trend in these values in terms of the change in the water molecule—ammonium ion interaction brought about by the substitution of an alkyl group for a hydrogen atom. A bulky alkyl group prevents the close approach of a water molecule which would otherwise be "frozen" in the first solvation shell by the ionic charge. Therefore, three alkyl groups effectively exclude a greater number of water molecules than one or two such groups. This explanation does not take into account any differences in the water molecule—alkyl group interactions which may be caused by the introduction of a charge on the molecule. Such interactions may be quite important. The reaction in which hydrogen ion and trimethylamine associate is accompanied by an entropy change of +15.3 e. u. Since the absolute value of $\bar{S}°_{H^+}$ is approximately −2 e. u. (*5*), the value of $\bar{S}°_{HN(CH_3)_3^+}$ − $\bar{S}°_{N(CH_3)_3}$ is approximately +13 e. u. A value as positive in magnitude as this is surprising, since this is probably close to the value of the difference between the entropies of solution of gaseous trimethylammonium ion and gaseous trimethylamine. As was pointed out in the comparison of the entropy of solution of two mols of argon gas and the sum of the entropies of solution of one mol each of potassium ion gas and chloride ion gas, factors other than charge-water molecule interactions play an important role in determining the entropy of dissolved substances. This is again indicated here; less freedom is lost by the system when gaseous trimethylammonium ion is dissolved in water than when gaseous trimethylamine is dissolved.

The trend of the $\Delta S°$ values with increasing chain length of the alkyl group is shown in Table 5. It is seen that the $\Delta S°$ values become less positive as the alkyl group chain length becomes greater. Evans and Hamann (*13*) discuss this; they attribute this to the loss, by the alkyl groups, of some freedom in the ion which they had in the neutral molecule. Kirkwood (*14*) has pointed out that groups of low dielectric constant embedded in a medium of high dielectric constant are repelled by charge. This would force the alkyl groups in the ion to stretch out; they would, thus, have less freedom than they do in the neutral molecule. This effect would become greater with increasing chain length.

In contrast to these reactions for which the $\Delta S°$ values were positive in every case, a selection of association reactions of a molecule and an ion in which the ΔS values are negative are presented in Table 6. These reactions differ from those already considered in one important respect. Hydrogen ion appeared as a reactant in all of the reactions of ammonium ion formation. Since the value of the entropy of hydrogen ion is more negative than that of any other cation of charge +1, reactions in which hydrogen ion disappears

TABLE 5

Reaction	*Temp.*	$K \times 10^{-10}$	ΔH(kg.-cal.)	$\Delta S°$(e. u.)	*Ref.*
$H^+ + CH_3NH_2 = CH_3NH_3^+$	25°C.	4.16	−13.09	+4.7[a]	(12)
$H^+ + C_2H_5NH_2 = C_2H_5NH_3^+$	30°C.	2.84	−13.58	+3.1	(13)
$H^+ + C_3H_7NH_2 = C_3H_7NH_3^+$	30°C.	2.23	−13.85	+1.7	(13)
$H^+ + C_4H_9NH_2 = C_4H_9NH_3^+$	30°C.	2.59	−14.07	+1.3	(13)
$H^+ + (CH_3)_2NH = (CH_3)_2NH_2^+$	25°C.	6.21	−11.86	+9.5[a]	(12)
$H^+ + (C_2H_5)_2NH = (C_2H_5)_2NH_2^+$	30°C.	6.32	−12.77	+7.2	(13)

[a] These values become 4.6 and 9.1, respectively, when corrected to 30° C. (*13*).

TABLE 6

Reaction	$K_{298°}$	ΔH(cal.)	ΔS(e. u.)	Ref.
$I^- + I_2$ (aq.) $= I_3^-$	710	−5,100	− 4	(15)
$Ag^+ + C_6H_{10}$[a] (aq.) $= Ag(C_6H_{10})^+$	79	−5,800[b]	−11	(16)
$Ag^+ + 2NH_3$(aq.) $= Ag(NH_3)_2^+$	1.7×10^7	−13,400	−11.9	(17)
$Fe^{++} + 3$Dipy[c] $= Fe(Dipy)_3^{++}$	1.2×10^{17}	−24,400	~0	(18)

[a] Cyclohexene.
[b] Derived from the temperature coefficient of K between 0 °C. and 25 °C.
[c] $\alpha\alpha'$ Dipyridyl.

may inherently have a more positive entropy change. Too many other differences exist between these groups of reactions to assert that this postulate is proved by these data.

Whether positive or negative, the $\Delta S°$ values for reactions of an ion and a neutral molecule are generally not large and, therefore, if an extremely stable species is formed in an association reaction of this type it is probably formed with the evolution of heat.

REACTIONS OF IONS OF OPPOSITE CHARGE SIGN

More regularity seems to exist in the values of the $\Delta S°$ of the reactions in which ions of opposite charge sign associate. A reaction of this type which has been widely studied is the reaction of hydrogen ion and the anion of a weak acid. Important contributions dealing with the general aspects of this subject are the papers by Pitzer (*19*), Everett and Wynne-Jones (*12*), Magee, Ri, and Eyring (*20*), and Harned and Owen (*21*). Data selected to illustrate the influence of a number of factors on the entropy changes in reactions of this type are presented in Table 7. It is seen that in many of the reactions in which a hydrogen ion associates with a singly charged anion, the $\Delta S°$ value is close to +22 e. u. even though acids of varying strength are considered.

It has been pointed out by Evans and Hamann (*13*) that the trend with alkyl chain length in the $\Delta S°$ values for the association of hydrogen ion and carboxylate anions is in the direction which can be explained in the same way as were the data for the mono- and dialkyl amines. That is, the alkyl group has more rotational freedom in the neutral molecule than in the ion.

As might be expected, the value of $\Delta S°$ for the association of a hydrogen ion with the glycine anion is not as positive as +22. (The values for other amino acids do not differ markedly from that for glycine.) In this case, the resulting molecule, while neutral, exists in the zwitter ion form, and thus still exerts powerful attractive forces on the solvent water molecules, just as did the separated ions. If one assumes that the carboxylate group–water molecule interactions are not altered particularly by the association of the hydrogen ion at the amine end of the molecule, the value of $\Delta S°$ for the association of hydrogen ion and the glycine anion might be expected to be similar to the values observed in ammonium ion formation reactions (see Tables 4 and 5). Actually, this is found to be the case. The other acids for which the $\Delta S°$ values are much less positive than +22 e. u. are also those in which the acid molecule has polarity due to groups in addition to the one acidic functional group.

The changes in entropy in the reactions of a hydrogen ion and an anion become progressively more positive as the charge on the anion becomes more negative. This is a reflection of the greater than first power dependence of the value of $-S°$ of the polyatomic anions on the charge (see Table 3). The role which the $\Delta S°$ plays in determining the ionization constants of these polybasic

TABLE 7

Reaction	$K_{298°}$	ΔH(cal.)	ΔS(e. u.)	Ref.
$H^+ + HCO_2^- = HCO_2H$	5.6×10^3	+40	+17.3	(12)
$H^+ + CH_3CO_2^- = CH_3CO_2H$	5.7×10^4	+100	+22.1	(12)
$H^+ + C_2H_5CO_2^- = C_2H_5CO_2H$	7.4×10^4	+170	+22.9	(12)
$H^+ + C_3H_7CO_2^- = C_3H_7CO_2H$	6.6×10^4	+700	+24.4	(12)
$H^+ + ClCH_2CO_2^- = ClCH_2CO_2H$	740	+1,150	+16.9	(12)
$H^+ + H_2NCH_2CO_2^- = H_3{}^+NCH_2CO_2^-$	6.0×10^9	−10,600	+ 9.2	(12)
$H^+ + ClO^- = HOCl$	2.5×10^7	−3,320	+22.8	(19)
$H^+ + ClO_2^- = HClO_2$	90	+4,100	+22.7	(19)
$H^+ + H_2PO_4^- = H_3PO_4$	130	+1,880	+16.0	(19)
$H^+ + H_2Cit^- = H_3Cit$[a]	1.34×10^3	−1,000	+11.0	(22)
$H^+ + CO_3^= = HCO_3^-$	1.8×10^{10}	−3,500	+35.2	(19)
$H^+ + SO_4^= = HSO_4^-$	83	+5,200	+26.3	(19)
$H^+ + HPO_4^= = H_2PO_4^-$	1.6×10^7	−800	+30.3	(19)
$H^+ + HCit^= = H_2Cit^-$	5.77×10^4	−580	+19.8	(22)
$H^+ + PO_4^{\equiv} = HPO_4^=$	8.9×10^{11}	−3,500	+43	(19)
$H^+ + Cit^{\equiv} = HCit^=$	2.49×10^6	+800	+32	(22)

[a] Cit. = Citrate.

TABLE 8
Thermodynamic Quantities for Complex Ion Formation Reactions[a]

	$K_{298}°$	ΔH(cal.)	ΔS(e. u.)	Ref.
$M^{++} + X^- = MX^+$				
$Cu^{++} + Cl^- = CuCl^+$	1.3	+600	+2.5	(23)
$Cd^{++} + Cl^- = CdCl^+$	25	+600	+8.5	(24)
$M^{+++} + X^- = MX^{++}$				
$Fe^{+++} + OH^- = FeOH^{++}$	5×10^{11}	−1,200	+50	(25)
$Fe^{+++} + O_2H^- = FeO_2H^{++}$	2×10^{9}, [b]	+1,800	+49	(26)
$Fe^{+++} + Cl^- = FeCl^{++}$	30	+8,500	+35	(25)
$Fe^{+++} + Br^- = FeBr^{++}$	4	+6,100	+23	(25)
$M^{++} + Y^= = MY$				
* $Zn^{++} + C_3H_2O_4^= = ZnC_3H_2O_4$[c]	5.6×10^3	−3,060	+27.5	(27)
* $Ba^{++} + S_2O_3^= = BaS_2O_3$	164	2,600	+18.8	(28)
$Ca^{++} + C_4H_4O_6^= = CaC_4H_4O_6$[d]	70	−3,510	−3.4	(29)
$M^{++} + R\equiv = MR^-$				
$Ra^{++} + Cit\equiv = RaCit^-$	110	~0	+9	(30)
$M^{+++} + Z\equiv = MZ$				
* $La^{+++} + Co(CN)_6\equiv = LaCo(CN)_6$	5.8×10^3	+1,300	+22	(31)
* $La^{+++} + Fe(CN)_6\equiv = LaFe(CN)_6$	5.5×10^3	+2,020	+24	(32)

[a] Some of the quantities refer to infinitely dilute solution; these are indicated with an asterisk to the left of the reaction equation. In the others, some fixed ionic strength existed which may be obtained from original reference. The significance of the ΔS value is less clear cut in the cases where the studies were made at a high ionic strength. This is due to the wide variation in observed values of $\bar{S}_2 - \bar{S}_2°$ for ionic solutes.

[b] Refers to 20 °C.

[c] $C_3H_2O_4^=$ = malonate.

[d] $C_4H_4O_6^=$ = tartrate.

acids is interesting. In the case of phosphoric acid, the successive ionizations become more endothermic but the change in ΔH is by no means as important as is the change in the $T\Delta S°$ term. In the case of citric acid, the trend in ΔH values is actually in the opposite direction of the trend of $\Delta F°$ values; the first and second ionizations are endothermic and the third ionization is exothermic.

Thus, it is seen that an association reaction involving a hydrogen ion and a negative ion is accompanied by a sizable increase in entropy. This is mainly a consequence of the much greater freedom which the water molecules enjoy in the field around the molecule compared to that which they have in the field of the separated ions. This entropy effect is not dominant, of course, in the case of strong acids. In these substances, which are completely ionized in solution, the association of the hydrogen ion and the anion, while presumably accompanied by an increase in entropy, is not accompained by an enthalpy change which favors association.

Fewer data exist for reactions in which a metal cation and an anion associate to give a complex ion or ion-pair. Data for this type of reaction are presented in Table 8.

It is indeed surprising that the $\Delta S°$ values for the reactions of lanthanum ion with ferricyanide and cobalticyanide ions are not more positive in view of their charges. These ion-pairs are believed to involve the hydrated lanthanum ion (*31*) (*32*); this is based primarily on the value of "*a*", the distance of closest approach parameter in Bjerrum's equation for ion association (*33*). The magnitudes of the $\Delta S°$ values substantiate this view. If the lanthanum ion exists in the associated ion-pair as the hydrated ion, the $\Delta S°$ value would be expected to be much less positive since the water molecules in the first sphere of coordination would not gain freedom when the ion-pair forms. It has been suggested by Schubert, Russell, and Myers (*30*) that in the ion pairs which the alkaline earth elements form with citrate ion, the metal ion is hydrated. The $\Delta S°$ values for the reaction of calcium ion with tartrate ion and radium ion with citrate ion seem to be consistent with this picture.

In contrast to this, it is seen that the formation of complex ions involving iron (III) is accompanied by a large increase in entropy. In these complex ions it seems reasonable to picture the anion in contact with the cation. No water molecules separate them; in fact, bonds with some covalent character are undoubtedly present. The values of $S°$ for the complex ions $FeOH^{++}$, $FeCl^{++}$, and $FeBr^{++}$ are 22.6, 21.9, and 27.8 respectively. These values are approximately the same, and therefore the trend in the ΔS values is due to the trend in the values of $S°$ of the anion. It would not be surprising if this were found to be generally true. If so, those halide complex ion systems in which the iodide complex ions are the most stable are ones in which the ΔH value must be becoming enough more negative as one goes from fluoride to iodide to offset the effect of the entropy term. Systems in which the order of stability of the halide complex ions is iodide > bromide > chloride > fluoride, such as the cadmium halides (*34*) and mercury (II) halides (*35*), are systems in which the bonding undoubtedly has a great deal of covalent character.

In general it might be expected that those anions which have large positive values of $S°$ would have only a slight tendency to form complex ions or ion pairs with metal ions. The anions, with known entropy values compiled by Latimer, Pitzer, and Smith (*11*), which

have the most positive values of $\bar{S}°$ are permanganate, perchlorate, chlorate, bromate, and nitrate. These anions are certainly not noted for their complex forming tendency. One factor which makes the entropies of these ions more positive is their rotational degrees of freedom but it also seems likely that these polyatomic anions are not very heavily hydrated. Thus the contribution to the stability of the complex ion or ion-pair which arises from the entropy term would not be as important in the case of these anions. Another factor, also related to the entropy change, which may play a role in determining the stabilities of complex ions involving polyatomic anions is the loss in rotational freedom which the anion itself must undergo when it becomes coordinated to a cation.

The values of the entropy change which are associated with various reactions in solution have been presented. Certain trends in these values and other generalizations have been pointed out. In some cases, these trends in the value of ΔS are amenable to simple rationalization; in other cases, this does not appear to be possible. The most important point, which the data illustrate, is the role which the water molecule-solute interactions play in determining the value of ΔS for a reaction in solution. The stability of many molecules and complex ions with respect to dissociation in solution is markedly influenced by the magnitude of the ΔS for the dissociation reaction.

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CIVIL SERVICE POSITIONS FOR STUDENTS

The United States Civil Service Commission has issued an announcement of a Student Aid Trainee examination which is open to college sophomores and juniors majoring in physical science or mathematics. Appointments will be for employment during school vacation periods or for periods of employment of students in cooperative courses. The positions pay $2,950 and $3,175 a year and are located in various Federal agencies in Washington, D. C. and vicinity. Applicants must have completed appropriate college study and must pass a written test. Students who expect to complete the required study by June, 1953 may apply. Full information regarding the training program and the requirements for applying are contained in the examination announcement.

RECENT HISTORY OF THE NOTION OF A CHEMICAL SPECIES[1]

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WE HAVE grown to accept the terms "element," "compound," and "mixture" as simple terms, simply defined. Timmermans, in a work[2] that is a must for every thinking chemist, shows how complex these terms really are.

The definitions of a chemical individual, and of chemical purity, have undergone recent revision in two directions. On the one hand, quantum and nuclear chemistry have challenged the doctrine that chemical elements are homogeneous entities. On the other hand, studies of the structure and stoichiometry of solids invite a change in our ideas of definite proportions in chemical combinations.

LAST ATTACK ON THE ATOMIC THEORY

Over a century ago Proust bested Berthollet in the mighty struggle that admitted Dalton's ideas into the fabric of chemistry. Today, we take these concepts for granted, and view this struggle as an old bygone.

It was as this century opened that a powerful attack purposing to banish the atomic theory was launched by Wilhelm Ostwald and Frantisek Wald.

Ostwald, the father of physico-chemical literature, one of the three musketeers of the ionic theory, and an eloquent and incisive arguer, was a figure of massive and honored prestige. Wald was a chemist of no mean attainments.[3] Ostwald opposed the atom on the principle that its existence was undemonstrated, and on the basis that the long chain of reasoning from postulated atomism to the phenomena of the laboratory was not altogether convincing. Wald held that the phase rule of J. Willard Gibbs could so define a phase of constant composition that the law of definite proportions would follow without atomistic assumptions.[4]

Ostwald, already a confirmed opponent of atomism, felt that Wald had made a constructive addition to his cause, and immediately joined forces with him.[5] Theirs was a noble enterprise; had it succeeded we would have had macroscopic systems defined in such a manner as to be invariant to future discoveries of the fine structure of matter. It was too noble to last; before long, cathode rays, radioactivity, and the Brownian movement indisputably established the particulate nature of matter. Ostwald half-recanted and Wald retreated into silence.

Out of this misadventure came an idea we would do well to think of more often. This is the concept of "hylotropy." A material that cannot be fractionated into components by a physical means is said to be "hylotropic" with respect to that means. A chemical individual exhibiting hylotropy to several physical means of differentiation over an appreciable range of thermodynamic coordinates (P, V, T, etc.) is defined as a "compound." To Ostwald and Wald an element was hylotropic for an infinite range of thermodynamic variables.

These definitions had two advantages over those then current, and over some that still clutter the textbooks of our time. First, a clearly macroscopic criterion was used to define materials in which the usual chemical interest is macroscopic. It serves little to use non-operational definitions in science. Is it not more to the point to tell a student that the material in a certain beaker cannot be fractionated without decomposition than to inform him pontifically that only one kind of molecule can be found in the liquid in the beaker?

Second, these definitions are in a form based upon thermodynamics, and under the sway of an idea of quantitative verification. Hylotropy can be determined by a Third Law entropy evaluation. We can sum up by saying that at least Ostwald and Wald had formulated a criterion of a chemical species.

COMPONENTIAL DIVERSIFICATION

Quantum and nuclear chemistry demonstrated that chemical elements were not hylotropic. Separation of monatomic metal vapors into spin components, diatomic gaseous elements into ortho-para states, elements into isotopic components, and the interconversion of nuclides have removed the doctrine of the immutability of chemical elements from the conceptual frame work of theoretical chemistry. We retain the idea of hylotropy to a means rather than the idea of infinite hylotropy in ordinary chemical operations.

These new discoveries leave our ideas as to how compounds are formed about the same as before. What they have added is a further choice of components. In this new chemistry we can, by selecting from three hydrogen isotopes, three carbon isotopes, and three oxygen isotopes, build a variety of methanols or formaldehydes. But, essentially, these would be methanols or formaldehydes respectively.

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[1] Presented at the 121st Meeting of the American Chemical Society, Buffalo, New York, March, 1952.

[2] TIMMERMANS, "Chemical Species," Chemical Publishing Co., New York, 1940.

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The operations of usual chemistry have given us the concept of purity on a mass basis. The operations of nuclear, radio-, and radiation chemistry lead to other concepts of purity. Since the Nuclear Age has reached a mass-production scale in fission, and promises to reach it in fusion, these concepts will rapidly become increasingly familiar. Since there is no reason to conclude that the art of exploiting breeder reactors differs from the other industrial arts of our technologic civilization, the amount, variety, and use of nuclidic products is due for a logarithmic increase.

In improving a hydrogen-bomb assembly line, we are concerned with the isotopic as well as the chemical purity of a sample of tritium. In the assay of a fission product from a breeder reactor run we are concerned with removing those elements whose radiation cannot be disentangled from that of the nuclide of interest by our assay devices; it is activity purity we are concerned with. If we want to determine an ultramicroscopic trace impurity by irradiation in an accelerator beam, we have to make certain that other similarly excitable material is absent or accounted for; we want activation purity. If we are projecting a new type of self-sustaining assembly with a severe space problem accompanying, we want nothing present that would interrrupt nuclear multiplication chains and are concerned with cross-section purity.

In the more complex world of tagged molecules and traced ions other ideas are met, but what has already been exemplified is paralleled. In all of these new chemicals the properties of interest are variables reflecting the mode and recency of origin. As their use increases, the bottle label will rival the handbook as the *vade mecum* of the bench chemist.

One aspect of nuclear chemistry differs from the more familiar ones of isotope and nuclide chemistry, and that is the chemistry of mixtures of nuclear isomers. Under some conditions a mixture of nuclear isomers is self-separating, we might almost say antihylotropic. The ordinary chemist will rarely encounter this type of "hot-atom" chemistry.

AGGREGATIONAL DIVERSIFICATION

Finding how "components" become "constituents" is a chief concern of chemistry. A change in the conceptualism of aggregation causes more upheaval to the chemist's mind than a mere diversification of components, such as the discovery of a new compound, element, nuclide, or nucleon.

The bitterest struggles in the history of chemistry have been those concerning aggregational notions. One need only recall radicals, types, molecules, ions, and tetrahedral carbon—each associated with polemic and bitterness. Of late, resonance has gone off to the cold war.

Perhaps another such struggle is brewing as a result of recent work in the solid state which seems to portend a modification of the law of definite proportions.

In the solid state we have materials whose molecular weight is either not directly determinable, or to which the concept of bounded microscopic structure cannot be extended. While some solids are composed of discrete ions and others of discrete molecules, there are a large number with fibril, sheet, or net structures of indefinite extent which have been respectively termed gigantic ions or gigantic molecules.

The stoichiometry of solids often yields no structural or componential information. We are often left in a position where we cannot reason unambiguously with constitutional questions short of a complete and tedious X-ray structural determination of a number of anomalous points in a phase diagram.

We frequently distinguish mixtures from compounds by comparing component properties with the properties of the aggregation. Persistence of component properties points toward mixture or solution. If we have a mixture, some component property usually varies with the amount of component present. In a compound on the other hand, we have so far believed that the constituent proportions cannot be varied; adding excess is supposed to yield a mixture. These constant proportions we attribute to valency, which possesses an integral character because discrete electrons are involved in chemical combination.

In metals, electrons as well as atoms act as structural members. Intermetallic compounds form at certain electron/atom ratios, *e. g.*, 21/12, 21/13, 21/14. These are devoid of the usual valence meaning.

We can sharply distinguish saltlike from metallic properties. Sodium tungstate is a typical salt. Partially reduced, it yields a "tungsten bronze," metallic in glitter and conductance. There is a variation of properties in the tungsten bronzes, but no component we can refer it to. We can refer it to a constituent, which is a different matter. We can note that sodium tungstite would have to be isomorphous with sodium tungstate, and that every intermediate state up to the tungstate would have to be similar to fulfill the requirements of an isomorphous series. The tungsten bronzes seem anomalous.

N. Kurnakow[6] first presented the idea that such entities are a new type of chemical species. He called ordinary compounds "Daltonides" (the French, mindful of the great debate, prefer "Proustide"), and compounds such as the tungsten bronzes, the corresponding molybdenum blues, and the non-stoichiometric chalcogenides he referred to as "Berthollides." Kurnakow predicted that further study would discover a vast number of berthollides.

E. Hüttig remarked[7] that with the atomic theory firmly accepted, we need no longer cling to old concepts affirmed to give confidence in it, but could now go on to accept the laws of classical stoichiometry as limiting laws.

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LABORATORY WORK IN A PHYSICAL SCIENCE COURSE[1]

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More and more interdepartmental science courses, for purposes of general education, are being planned or offered by colleges and universities. More and more chemists are being asked to participate in these classes. If the chemist turns a cold shoulder, the course will often be taught by others with whose point of view he has little sympathy. Participation of chemists in these interdepartmental science courses is not only desirable—it is urgent.

These interdepartmental courses are usually outlined especially for nonscience majors. *Such courses need not be superficial.* Chemists and other scientists who participate thoughtfully and enthusiastically *can* make them meaty courses *in science* rather than watered-down courses *about* science.

Laboratory work in such a course provides a problem with which many are wrestling. Two aspects of the problem need particularly to be considered. The first is the general-education nature of the courses. The usual laboratory work in the traditional departmental classes may not necessarily meet the needs of general education. The second aspect of the problem results from the breadth of the course. The laboratory methods and procedures appropriate to one of the sciences may not be at all suitable in the others.

Let us be specific: The physical science course at the University of Illinois draws material from the traditional fields of chemistry, physics, astronomy, and geology. Astronomy needs evenings at the observatory, geology needs field trips, chemistry needs a laboratory with test tubes and acids, while physics equipment would be damaged by acid fumes. Only a single student at a time can look through the observatory telescope, but geology field trips can be conducted in bus-load groups. A usual laboratory section, meeting at a regularly scheduled hour week after week, always in the same laboratory, is hopelessly inappropriate.

During the past 11 years the physical science staff at the University of Illinois has been experimenting with various laboratory exercises and procedures. The experimentation still continues, but the methods that have evolved so far are at least a great improvement over those with which we started in meeting our particular needs.

The physical science course at the University of Illinois is a rigorous one, designed particularly for general education purposes. It is one of several that can be taken by students in liberal arts and sciences, commerce, education, pre-journalism and pre-law, to fill a science requirement. It is a two-semester course in which the student earns four semester-hour credits each term. The class is scheduled for five 50-minute periods each week. The entire class (220 students last fall) registers for the same Monday-Wednesday-Friday lecture periods. Each discussion section of 15 to 20 students meets Tuesdays and Thursdays.

The Friday period is usually devoted to some activity other than lectures. About every third week there is an hour-examination, usually during the Friday period. Some kind of laboratory work takes the place of most of the other Friday lectures. The student does not sign up for a particular laboratory section when registering for the class at the beginning of the term. Instead, laboratory sessions are scheduled at appropriate times as needed. (These might involve evenings at the observatory or Saturday field trips, as well as usual week-day hours. With the exception of field trips, the laboratory sessions usually last 50 minutes, but may require outside study and writing. A few days before the exercise, a list of times for the laboratory sessions is announced, and each student signs up for the time that best meets his convenience. Only an appropriate number of students are permitted to choose any particular laboratory period. For some exercises, groups as large as 30 students can be handled; for other exercises the number signing for any particular hour may be limited to a maximum of 12. In general, for each of these laboratory exercises, a Friday lecture period is canceled. Those students who have no other time available during the week in which to do the laboratory work can then usually do it during that Friday period which was freed by the cancellation of the lecture.

In general, then, each student attends his physical science class at regularly scheduled hours Monday through Thursday. On Friday he may have an hour-examination or occasionally a lecture. Or in place of the Friday period he may have an evening hour at the observatory or a laboratory session at a time of his own choosing.

Some of the "laboratory" activities are quite different from the usual formal laboratory work familiar to chemists. Furthermore, some of the activities are carried on by the student on his own, outside of scheduled periods.

The course starts with an introductory lecture on stars and constellations, so that the students will begin watching them during the pleasant fall weather. It then leads into a study of mechanics, with the motions of the earth and their consequences being considered

[1] Presented at the 122nd meeting of the American Chemical Society, Atlantic City, September, 1952.

in particular. Mechanics and a brief discussion of electrostatics lead to a thorough study of atomic structure. The subsequent consideration of electricity and light (electromagnetic waves) is based on atomic structure. This ends the first semester. In the second term the fundamental principles of chemistry are studied, based solidly on the extensive background in atomic structure. A consideration of geology then applies both the chemistry and physics that have preceded. (Pleasant spring weather permits outdoor laboratory exercises and field trips.) The course then turns again to astronomy, particularly the understanding that light brings us concerning the nature of the stars, their compositions, temperatures, and motions. Finally, the year closes with a brief consideration of hypotheses of cosmic origins.

Throughout the course there is emphasis on "scientific method," or more exactly, on the fostering of a scientific attitude in the students. This naturally requires practice in accurate observation and in drawing objective conclusions. It is toward these ends that much of the laboratory work is directed. Another legitimate aim of the laboratory work is the accumulation of knowledge which will itself be intrinsically useful or will lead to greater understanding, appreciation, and pleasure.

The first "laboratory exercise" is usually a visit to the observatory. While awaiting their turns to see the moon or a planet through the telescope, the students go outside and begin to become acquainted with the brightest stars and constellations, as well as any planets that may be visible. During subsequent visits to the observatory the telescope is turned to other objects in the sky, while those students who are waiting go outdoors if they want additional help in learning the stars and constellations. Some of the observatory visits are optional, and for them no lecture time is canceled.

The students are asked to watch the changes that occur in the sky as a result of the earth's rotation and revolution. They are also asked to follow the independent motions of appropriate planets visible during the school year. Questions on the hour-examinations test the faithfulness and accuracy of their observations.

One astronomy exercise which well meets aims of the general education course is the following: Each student is asked to become able to name and point out in the sky any combination of 20 bright stars and/or constellations. Then, when he is ready, each class member is given an individual opportunity to point out to an instructor the stars and constellations he has learned. The quizzing is of course outdoors, right out under the stars, and takes about 10 to 15 minutes per student. This exercise has been carried through on a limited and voluntary basis so far, partly because of the time required for testing. However, a suitable flat roof-top, up above the campus lights, is being provided for us on one of the university's new buildings, and starting this fall, we plan to make this a required exercise. This assignment could be repeated in the second semester, since different stars are then visible.

When the sun is being studied in class, discussion sections are taken to the observatory on a bright day to see sun spots, the solar spectrum, etc.

The physics experiments deal with motion and force, heat and kinetic theory, electrostatics, cathode rays and electrons, magnetism and electromagnetic induction. (Additional experiments, such as sound and light, could of course be added.) The equipment is set up, ready for use, so the student loses no time in assembling apparatus. He spends the hour making observations, and does his calculations on the outside. We have our own physics laboratory.

The course does not possess a chemistry laboratory, so a freshman chem. lab. must be borrowed, and the number of chemistry exercises is limited to two. This is enough, however, for the students to see what a chemistry laboratory is like, and to get some first-hand acquaintance with precipitates, indicators, etc.

The two chemistry laboratory exercises are called "acids, bases, salts"; and "metals and non-metals." They deal with the properties of these classes of compounds, and include the construction of an electromotive series and the placement in it of an unknown metal. Each student is given an individual unknown. He is not asked to identify it but merely to discover where it fits into the electromotive series he has constructed. Sodium, calcium, magnesium, zinc, iron, lead, hydrogen, copper, and silver are the elements which he arranges in an activity series on the basis of his experiments. Then manganese, cadmium, cobalt, tin, and bismuth, in as many different forms and appearances as can be obtained, are the metals used for unknowns. The exercises are graded, not according to where the element ideally should fit into the series, but where the actual samples do fit on the basis of the properties which the student can observe.

These chemistry exercises are done on days when there is a vacant freshman laboratory. A set of the needed equipment (test tubes, beakers, burner, etc.) is placed on each desk, and the required chemicals are put nearby. Replenishments and unknowns are available on a cart in the middle of the laboratory. The students do not need to go to the storeroom for anything. They therefore do not bother the chemistry storeroom attendant, and they lose no time waiting in line. The students work in pairs, and by our having everything at hand on their desks they can accomplish as much in a single hour as chemistry students usually get done in a two- or three-hour period.

One of the geology exercises deals with the observation of minerals in museum cases. Another asks the student to locate and identify various kinds of rocks in the university rock garden and rocks used as building stones on the campus. An exercise on land forms deals with the stereoscopic study of aerial photographs, and asks the student to classify valleys so observed as young, mature, old, rejuvenated, etc.; classify regions similarly; classify craters; locate deltas, terraces, etc.

The field trip is usually a half-day, 70-mile trip by bus (school buses are hired), with about six or seven

stops (at road cuts, a limestone quarry in which a glacial pavement is beautifully shown, a kame being excavated as a small gravel pit, etc.). An optional alternative is a full-day, 175-mile trip which adds a visit to an open-pit coal mine and Turkey Run State Park in Indiana.

One of our best exercises does not take any time from lecture. It is done by the student on the outside. He is asked to make a collection of rocks and rock structures, identify and label them, and hand them in for scoring. The rocks can include any ten different kinds he can find and identify. He is asked to find examples of any five of the following structures: concretion, cross-bedding, dike, exfoliation, foliation, fossil, geode, glacial striae, sill, stratification, vein. He may substitute other structures if he finds good examples. Mimeographed directions for the exercise are pasted onto a one-quart paper cylinder, such as is used for ice cream, by means of Scotch Tape. We provide this container, rather than have the students hand in their collections in paper sacks, candy boxes, or what not. The strong and uniform packages are much easier for us to handle. Grading the collections is not burdensome. The exercise has proved to be a very worthwhile one, and one which the students enjoy. Many of the students assemble excellent collections. Quite a number of the examples are found during the field trip, and this search for specimens adds even greater zest to the trip than it already has.

The more formal laboratory exercises are in general mimeographed, with space left for write-in answers. The usual difficulties can of course, arise. Students can copy many answers from other students, and scoring of the exercises can be very time-consuming. We are getting at least partly around these difficulties, however, by doing little routine scoring of the papers and by testing for mastery of the important points through examination questions instead.

While some of the exercises mentioned above are original with us, others are quite traditional in subject matter. Here we have made a change from usual procedures, however, in the mechanics of scheduling the laboratory sessions. Abandoning the rigid registration in formal laboratory sections which meet at time-table hours throughout the term, and having the students sign up for the individual exercises in groups of appropriate size at appropriate times, has proved advantageous in this course. This system has maximum flexibility, and is probably as efficient in use of facilities and instructor time as any satisfactory method of handling such varied laboratory work could be.

We shall be glad to give further information or copies of the laboratory exercises to any who might want them.

A DOUBLE-POSTAL-CARD METHOD FOR REQUESTING REPRINTS

GERALD J. COX and JESSICA WITTEMAN NATHANS
University of Pittsburgh, Pittsburgh, Pennsylvania

WE HAVE obtained reprints, or separates, from authors in response to our requests by letter or postal card, but if reprints were not available we have usually not been able to obtain that information. We have found that by use of a return postal card, either dispatched as part of a double card or enclosed with a letter, that we have excellent success in learning, without cost to the author and with little effort on his part, whether reprints are available.

For requests by postal card within the United States and for Alaska, Canal Zone, Hawaii, Puerto Rico, and the Virgin Islands we have used the domestic double card; for requests in Canada, Central America, Cuba, Mexico, Philippine Islands, South America and Spain we have employed the 2-cent (4-cent double) international postal card; for all other countries, the 3-cent (6-cent double) international card has been used. We have, however, found it necessary to print on the return portion of the international card "Postage prepaid in all countries. Detach and post" as some of our respondents have unnecessarily placed their national stamps on the return cards.

The text, in English, for the return cards, is as follows:

.....Reprint is (reprints are) being sent
.....Reprint (s) will be sent when available
.....No reprints were obtained
.....Supply of reprints exhausted
.....Other reason.....
Date..... Signed.....

We type the name of the author, to whom the request is addressed, on the reply card and add a serial number for identification with our record. The latter consists of a single carbon copy of all material typed on the card.

Our cards have been prepared by printing from set type or from typescript by the usual duplicating processes.

In the table are shown the results obtained from 266

requests using the double postal card from May 7, 1951 through June 5, 1952.

Frequency of Response to Requests for Reprints

Type of double postal card	*Number of requests*	*Number of reprints*	*Number of responses without reprints*	*No response of any kind*
Domestic	211	140	28	43
International, 4¢	10	10	0	0
International, 6¢	45	29	3	13
Totals	266	179	31	56

The *chi*-square value from the table for response versus no response is 0.3, indicating no significant differences in the effectiveness of the domestic and international double cards.

As shown in the table, we had information from 31 of 87 authors who returned no reprints, or 36 per cent. We made no comparable study using single postal cards but, obviously, except for those few authors who would write a letter, there would be no information about the non-return of reprints.

Many authors have returned the unused reply card with the reprint requested, permitting us to reclaim part of the cost of these postal cards. Other respondents have written brief messages on the reply cards, thus giving us an unexpected return of news.

(*Note:* The authors have ordered 250 reprints of this article.)

FRAGMENTS OF CHEMISTRY

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10. PHYSICAL PROPERTIES OF METAL SOLUTIONS

Our knowledge of the physical properties of solutions of the alkali and the alkaline earth metals in liquid ammonia and in the lower, primary, aliphatic amines is still very incomplete. These solutions are truly unique; they constitute a link between electrolytes, on the one hand, and metals, on the other. Although solutions of the metals in liquid ammonia have been known for 88 years, it is a surprising fact that they have attracted but little attention and only a comparatively small number of investigators have been concerned in the development of this interesting and important field.

Dilute metal solutions exhibit a fine blue color; concentrated solutions exhibit metallic reflection somewhat of a copper or bronze color. The solutions are excellent conductors of an electric current. In dilute solutions, the current is carried, in part, by the positive ions of the dissolved metal; in larger part, it is carried by a negative carrier which is the same for all metals. This carrier has been identified as the negative electron which, in dilute solution, is in some way associated with ammonia molecules. In a dilute sodium solution, $^1/_8$ of the current is carried by sodium ions and $^7/_8$ by electrons. With sodium, potassium, and lithium in liquid ammonia, the metal surfaces of the electrodes are perfectly reversible with respect to electrons at all concentrations.

As concentration increases, the equivalent conductance decreases, much as it does for ordinary salts; at about 0.05 *N*, the conductance passes through a minimum. As concentration increases above that of the minimum, the conductance increases at an increasing rate with respect to concentration until the saturation concentration is reached where the conductance is comparable with that of metals.

The limiting equivalent conductance of a sodium solution at infinite dilution is 1020; its conductance at the minimum is 475, that of the saturated solution is 800,000.

The specific conductance of a saturated solution of sodium in liquid ammonia at –33.8° is 5047; that of mercury at 20° is 10444. In other words, the specific conductance of the saturated sodium solution is approximately one half that of mercury. However, the saturated solution contains 5.7 molecules of ammonia per atom of sodium. The atomic conductance of the saturated sodium solution is 0.800×10^6 while that of mercury is 0.156×10^6. Thus, the atomic conductance of the saturated sodium solution is more than five times that of mercury; it is more than one-seventh that of metallic sodium. There can be no question as to the metallic nature of concentrated solutions of metals in ammonia.

It has been shown that the fraction of the current

carried by the electrons, which is $^7/_8$ for sodium at low concentrations, increases with concentration, at first slowly, and then, at concentrations above 0.05 N, more rapidly. In the neighborhood of 1.0 N, the carrying capacity of the negative ion is several hundred times that of the sodium ion.

PROBLEMS CONCERNING METAL SOLUTIONS

The foregoing is intended to supply some background for that which follows. Here we shall attempt to present some problems in the field of metal solutions that are urgently in need of further investigation.

Conductance Measurements. By way of introduction, it may be noted that the most reliable data that we have today concerning the conductance of dilute metal solutions in ammonia date back some 45 years. It would seem that, with the improved facilities and techniques of today, somebody ought to be able to make measurements more precise than those that could be made half a century ago.

Let us first consider dilute metal solutions. The most and, indeed, the only reliable data that we have are for sodium in liquid ammonia at –33.5°. For qualitative purposes these data are satisfactory, but they lack the precision necessary for an analysis of the problem from a quantitative point of view. We have data relating to potassium at intermediate concentrations but none such for dilute solutions. There are some data for lithium at intermediate concentrations but none at all for dilute or concentrated solutions. There are some data for mixtures of sodium and potassium that indicate that such solutions might be measured successfully.

There are no data as to the conductance of rubidium and there are only limited data for cesium in liquid ammonia at –70°. We have no data relating to the conductance of the metals of the alkaline earths. With the exception of potassium and cesium, there are no data as to the conductance of any metals in the amines. The conductance of potassium in methylamine has been measured over a rather narrow concentration range and that of cesium to approximately 1.0 N. There are no reliable data at concentrations much below 10^{-3} N.

At higher concentrations, we have reliable data for sodium and potassium in ammonia from about 0.13 N to the saturated solutions. Probably, the data for sodium and potassium between 0.1 N and 0.001 N are not greatly in error. We have data for lithium between 0.01 N and 2 N that seem fairly satisfactory but we have nothing at higher or lower concentrations. There are some data on the conductance of lithium in ammonia in the solid state, including measurements of the Hall effect. The precise nature of the solid phase has not been established.

Temperature Coefficient of Resistance. We have satisfactory data for the resistance temperature coefficient of sodium and potassium at temperatures below −33° and concentrations above 0.13 N. We have only preliminary data for the temperature coefficient of dilute solutions of sodium at higher temperatures. There are some data on the temperature coefficients of sodium and potassium solutions at intermediate concentrations and temperatures.

At 0.13 N, the resistance temperature coefficient for sodium in the temperature interval −33° to −40° is 1.52%/deg. For potassium in the interval −33° to −45° it is 1.42%. As the concentration increases, the temperature coefficient increases to a maximum of 3.6% for sodium at 0.85 N and 4.6% for potassium at 1.1 N. At concentrations above that of the maximum, the coefficient falls off sharply reaching values of 0.0656% for a saturated solution of sodium and 0.0438% for potassium. It is to be noted that the resistance decreases with increasing temperature in all cases. However, if we could obtain solutions of higher concentration, we might expect the coefficient to change sign.

The differential temperature coefficient $d\ln R/dT$ is constant and independent of temperature with the exception of potassium solutions at a concentration of 1.1 N, where the $\ln R$-T curve exhibits a slight curvature at lower temperatures. For a dilute solution of sodium, of unspecified concentration, the $\ln R$-T curve is linear from −33° to +85° within the limit of experimental error. The temperature coefficient is 1.87%. The differential temperature coefficient of sodium at intermediate concentration (0.04—0.004 N) is 2.0%; that of potassium in the same concentration range is 2.9%. The temperature coefficient for potassium in methylamine (0.01–0.001 N) is 2%, that of cesium (0.1—0.001 N) is 2.4%. The temperature interval covered was from −30° to −48°, except in the case of sodium, where measurements have been carried out for the interval −48° to −70°.

The temperature coefficient of solutions of sodium and potassium in ammonia at −33° appears to have a minimum value of approximately 1.5% at 0.13 N; toward higher concentrations the coefficient has a maximum value of approximately 4% in the neighborhood of 1.0 N, and decreases thereafter to a value of the order of 0.05% for the saturated solutions. At lower concentrations, the temperature coefficient has a value of the order of 2% and the temperature coefficient remains constant for the interval −33° to +85°.

At −34° the temperature coefficient of a 4×10^{-4} N solution of sodium bromide is 1.12%, at 1×10^{-3} N it is 1.00%, and at 1×10^{-2} N it is 0.84%. At lower temperatures, the increased conductance of dilute salt solutions parallels the increased fluidity of ammonia which is 1.1%. At concentrations ranging from 0.1 to 0.01 N, the conductance of salts passes through a maximum in the neighborhood of 25°. Thereafter, it decreases and the temperature coefficient, accordingly, is negative. The temperature behavior of salts is satisfactorily accounted for by the effect of temperature on the viscosity of the solvent, on the one hand, and on the ion-ion pair equilibrium on the other.

The wide divergence in the temperature behavior of

metal and of salt solutions clearly indicates that the viscosity of the solution plays a minor role, if any, in the conductance of metal solutions. It would seem that the observed results could be accounted for only by the effect of temperature on the interaction between electrons and solvent molecules. It seems not unlikely that the conductance change of metal solutions with concentration may have to be accounted for in a similar manner.

Volume Changes Accompanying Solution. The density of liquid ammonia at −33.2° is 0.6816; the densities of lithium, sodium, and potassium are, respectively, 0.534, 0.971, and 0.870. The saturated solutions of the same metals contain, respectively, 3.61, 5.37, and 4.87 mols of ammonia per atom of metal and the densities of these solutions are 0.490, 0.578, and 0.638, respectively. The volume change, ΔV, accompanying the process of solution to saturation for the three metals has the values 34.2, 41.0, and 27.3 cc. per atom. The volume change accompanying the process of solution is rather large and varies from metal to metal.

The volume change for sodium increases as the NH_3/Na ratio increases and reaches a maximum of 43.4 cc. at 11.25 mols of ammonia per atom of sodium. Thereafter, the volume change, ΔV, decreases and reaches a value of 39.4 cc. at NH_3/Na = 64.1. It would appear that the ΔV approaches a value somewhat below 39 cc. at lower concentrations of sodium.

For potassium, the ΔV *vs.* NH_3/K curve is similar to that for sodium; the maximum, however, is lower and is only 29.8 cc. at NH_3/K = 10.5. For NH_3/K = 34, ΔV = 24.7.

The ΔV-concentration curve for lithium differs greatly from that for sodium and potassium. The curve rises continuously from a value of 34.2 for the saturated solution to a maximum value of 46.4 in the neighborhood of NH_3/Li = 29.3; the maximum is very flat. At the concentration NH_3/metal = 29.3, the ΔV values for lithium, sodium and potassium are, respectively, 46.4, 41.4, and 25.6; the densities are 0.639, 0.655, and 0.670, respectively. It is interesting to note that at NH_3/metal = 29.3, the volumes of the solutions containing one gram atom of metal are, respectively, 792, 804, and 797 cc. For the same ratio of ammonia to metal, the volume of a solution of potassium differs from that of lithium by only 5 cc. The difference in the densities of these two solutions is due chiefly to the difference in the weight of their atoms.

It would be of interest to have data for the volume changes of other metals, particularly cesium and rubidium. However, a more important problem is that of determining the volume change for dilute solutions. At this time we have no reliable data for dilute solutions. Volume changes have been reported for dilute sodium solutions that run from 60 to 600 cc. per atom. The lower value is probably of the right order of magnitude. The coefficient of expansion of ammonia at −33° is 0.0018; for 100 cc. of ammonia the expansion would be 1.8 cu. mm. for a temperature change of 0.01°. If one milatom of metal were dissolved in 100 cc. of ammonia we might expect a volume change of the order of 50 cu. mm. If temperatures were controlled to 0.01°, the volume change could be determined with a precision of approximately 5 per cent. Such measurements should present little difficulty in this day and age.

Some writers are inclined to ascribe the whole volume change to the electron. This does not seem warranted. When ordinary salts are dissolved in ammonia, volume changes occur which are of the order of magnitude of those observed with metals. For example, with sodium bromide and a NH_3/NaBr ratio of 350, there is a volume contraction of 25.6 cc. per mol. With increasing concentration, the volume change diminishes, changes sign, becomes positive, and thereafter increases with increasing concentration. For the ratio NH_3/NaBr = 45, there is a volume expansion of 16 cc. per mol.

We do not know how a given ion affects the volume change that is observed when its salt dissolves in a given solvent. We only know the resultant change due to two ions. This holds for metals as well as for salts. The observed effects, moreover, are dependent on concentration. Precise data of volume changes for the different alkali metals at low concentrations might conceivably serve to throw some light on this problem.

Magnetic Properties. Simon Freed's very careful measurements of the magnetic susceptibility of solutions of potassium, calcium, and barium in liquid ammonia throw much light on the nature of metal solutions. He has measured the magnetic susceptibility of potassium from low concentrations to 0.43 *N*. At the lowest concentrations the susceptibility approaches that of a free electron gas, at higher concentrations the susceptibility falls off to very low values.

The results indicate that in dilute solutions the electrons exist as independent, elementary magnets, having one-half unit of spin; their state may be accounted for by classical statistics. At higher concentrations the electrons interact with one another and their spins become paired.

Recently it has been reported that the metal solutions exhibit magnetic resonance to a marked degree. Details seem not to have been published. Further measurements along these lines give promise of throwing added light on the nature of the metal solutions. It would be of interest to measure the magnetic susceptibility of metals in methylamine and ethylenediamine.

Transport Numbers. We have data relating to the transport numbers of the ions in solutions of sodium in ammonia at −33°. The method employed to determine the transport numbers was to measure the electromotive force between two solutions whose concentrations were in the approximate ratio of 2 : 1. Assuming that the energy of the cell is supplied entirely by the sodium ion in going from the higher to the lower concentration, in which case it is assumed that the transfer of the electron from one solution to the

carried by the electrons, which is $^7/_8$ for sodium at low concentrations, increases with concentration, at first slowly, and then, at concentrations above 0.05 *N*, more rapidly. In the neighborhood of 1.0 *N*, the carrying capacity of the negative ion is several hundred times that of the sodium ion.

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It would be of interest to have data for the volume changes of other metals, particularly cesium and rubidium. However, a more important problem is that of determining the volume change for dilute solutions. At this time we have no reliable data for dilute solutions. Volume changes have been reported for dilute sodium solutions that run from 60 to 600 cc. per atom. The lower value is probably of the right order of magnitude. The coefficient of expansion of ammonia at −33° is 0.0018; for 100 cc. of ammonia the expansion would be 1.8 cu. mm. for a temperature change of 0.01°. If one milatom of metal were dissolved in 100 cc. of ammonia we might expect a volume change of the order of 50 cu. mm. If temperatures were controlled to 0.01°, the volume change could be determined with a precision of approximately 5 per cent. Such measurements should present little difficulty in this day and age.

Some writers are inclined to ascribe the whole volume change to the electron. This does not seem warranted. When ordinary salts are dissolved in ammonia, volume changes occur which are of the order of magnitude of those observed with metals. For example, with sodium bromide and a NH_3/NaBr ratio of 350, there is a volume contraction of 25.6 cc. per mol. With increasing concentration, the volume change diminishes, changes sign, becomes positive, and thereafter increases with increasing concentration. For the ratio NH_3/NaBr = 45, there is a volume expansion of 16 cc. per mol.

We do not know how a given ion affects the volume change that is observed when its salt dissolves in a given solvent. We only know the resultant change due to two ions. This holds for metals as well as for salts. The observed effects, moreover, are dependent on concentration. Precise data of volume changes for the different alkali metals at low concentrations might conceivably serve to throw some light on this problem.

Magnetic Properties. Simon Freed's very careful measurements of the magnetic susceptibility of solutions of potassium, calcium, and barium in liquid ammonia throw much light on the nature of metal solutions. He has measured the magnetic susceptibility of potassium from low concentrations to 0.43 *N*. At the lowest concentrations the susceptibility approaches that of a free electron gas, at higher concentrations the susceptibility falls off to very low values.

The results indicate that in dilute solutions the electrons exist as independent, elementary magnets, having one-half unit of spin; their state may be accounted for by classical statistics. At higher concentrations the electrons interact with one another and their spins become paired.

Recently it has been reported that the metal solutions exhibit magnetic resonance to a marked degree. Details seem not to have been published. Further measurements along these lines give promise of throwing added light on the nature of the metal solutions. It would be of interest to measure the magnetic susceptibility of metals in methylamine and ethylenediamine.

Transport Numbers. We have data relating to the transport numbers of the ions in solutions of sodium in ammonia at −33°. The method employed to determine the transport numbers was to measure the electromotive force between two solutions whose concentrations were in the approximate ratio of 2 : 1. Assuming that the energy of the cell is supplied entirely by the sodium ion in going from the higher to the lower concentration, in which case it is assumed that the transfer of the electron from one solution to the

other involves no osmotic work, the transport number n of the sodium ion may be approximated. Measurements carried out in the concentration range 2×10^{-3} N to 1.0 N yielded values of $(1-n)/n$ increasing from 7 in the most dilute solution to 276 in the most concentrated solution.

With decreasing concentration the ratio $(1-n)/n$ appears to approach a limiting value in the neighborhood of 7. The best value we have for the limiting conductance of metallic sodium is 1020 and the best value for the conductance of the sodium ion is 130. On this basis, the limiting value of $(1-n)/n$ should be 6.8. The results of transport number measurements are in accord with measurements of other properties within the experimental error.

It would seem that, today, it should be possible to obtain more precise data for the transport numbers of the ions of metals in ammonia. Moreover, it would be of interest to have values for other metals such as lithium, potassium, and barium in ammonia as well as in the amines.

Photoelectric Effects. Concentrated solutions of lithium in liquid ammonia have been shown to exhibit a photoelectric effect. Solutions of sodium in liquid ammonia have been studied at lower concentrations and it has been shown that electrons are liberated by light from the surface of such solutions. It appears that, at lower concentrations, the electrons are bound to some center and are not free. It might be of interest to study metals other than sodium.

Absorption Spectra. Solutions of sodium in liquid ammonia in the dilute region have been studied. There is a marked transmission toward shorter wave lengths and Beer's law appears to apply. The absorption spectra of concentrated solutions have not been studied; according to visual observation thin films of concentrated solutions are blue. There are some data on the absorption spectra of metals in methylamine. Beer's law does not hold generally. Further studies are much needed, particularly in concentrated solutions.

Stability of Metal Solutions. Solutions of metals in liquid ammonia are in a metastable condition. In the presence of catalysts, ammonia reacts with the metals according to the equation:

$$M + NH_3 \rightarrow MNH_2 + \tfrac{1}{2}H_2 \qquad (1)$$

We cannot say whether or not the metals would react with ammonia in the complete absence of catalysts; in other words, whether reaction occurs in the liquid phase or only on the surfaces of solids. We do not know to what extent reaction between metals and ammonia is increased with increasing temperature. What we do know is that most solids catalyze reaction, particularly oxides and finely divided metals. Even bright metal surfaces catalyze the reaction to an appreciable extent. We know that if the glass container of the solution is carefully cleaned and the atmosphere is rigidly excluded, very little reaction occurs. However, when working at very low concentrations, the amide reaction is usually a source of difficulty. It has been reported that the amide reaction takes place more readily with cesium than with other alkali metals.

Up to now nobody has made a systematic investigation of the amide reaction with a view to finding means whereby solutions of highest stability might be obtained. Such a study is a necessary prelude to a study of dilute solutions of the metals in ammonia or in the amines.

Some Uncultivated Fields. The chemistry of metal solutions is replete with problems. We know nothing about the phase relations in solutions of rubidium at lower temperatures. Indeed, we know nothing about any of the physical properties of solutions of rubidium. Solutions of sodium, potassium, and lithium separate into two liquid phases at lower temperatures; cesium solutions appear not to exhibit this phenomenon. Such information as we have indicates that the properties of cesium solutions differ markedly from those of the lower members of the alkali metal group. The properties of the ammoniates of the alkaline earth metals might bear investigation. Barium might have sufficient solubility so that various properties of its solutions could be studied.

However, the solutions that are in greatest need of study are those of the alkali metals in the amines: methylamine, ethylamine, and ethylene diamine. About all that we know regarding solutions in these solvents, as of now, is that some alkali metals are soluble in some of the amines, that their solutions have a blue color, and that solutions of potassium and cesium in methylamine have a conductance curve somewhat similar to that of sodium in ammonia. Ethylene diamine, in particular, should be studied since this liquid boils at 115° and appears to be a good solvent for metals. This solvent might prove of particular value in studying the properties of metal solutions at higher temperatures.

We have good reason for believing that the electron in the more dilute ammonia solutions interacts with the solvent molecules. In another solvent, the interaction should be modified and a study of such solutions might well throw light on the interaction of electrons with solvent molecules.

The effect of small additions of ammonia on the properties of solutions of metals in the amines would be of interest. Sodium is practically insoluble in ethylamine; its solubility is greatly increased by the addition of small quantities of ammonia. A study of the phase relations in mixtures of amines and ammonia might yield valuable results.

Concentrated solutions of lithium might be studied from near liquid air temperature to 60°C. The vapor pressure of a saturated lithium solution is only 3.2 mm. at −33°; it reaches the value of one atmosphere at about 60°. It would be a comparatively simple matter to measure the conductance of concentrated lithium solutions over a wide range of temperatures.

When solutions of the quaternary alkyl ammonium salts are electrolyzed in ammonia, a blue colored so-

lution is formed. Visually, such solutions are indistinguishable from those of the alkali metals. Here we are dealing with what is, in effect, a synthetic, organic metal. It should be possible to develop convenient methods whereby these groups could be obtained in solution in ammonia and, perhaps, the amines. The stability of such groups should be studied. Altogether, the metal solutions present an interesting and important field for investigation, the surface of which, up to now, has scarcely been scratched.

STATE OF METALS IN SOLUTION

The high conductance and the low resistance temperature coefficient of concentrated metal solutions in ammonia indicate clearly that the state of electrons in these solutions is much the same as that of electrons in ordinary metals, particularly liquid metals. The specific conductance of a saturated sodium solution is one-half that of mercury and its atomic conductance is five times that of mercury. The temperature coefficient of resistance of a concentrated potassium solution at $-33°$ is $+0.0438\%$. In this connection, it may be noted that the resistance temperature coefficient of mercury at 20°C. and constant pressure is $+0.089\%$; the temperature coefficient at constant volume is -0.069%. In what manner the ammonia (5.37 mols/atom Na) affects the state of the electrons, other than as diluent, is unknown.

In dilute solutions of metals in ammonia, the electrons interact with solvent molecules. Owing to this interaction, the mobility of electrons is cut down to where it becomes comparable with that of ordinary ions. In dilute sodium solution, the mobility of the electron is approximately seven times that of the sodium ion. By way of comparison, the conductance of the hydrogen ion in water is seven times that of the sodium ion at 25°. However, it is not correct to say that the conduction process in dilute metal solution is an electrolytic one; only one-eighth of the current is carried by the sodium ions, and therefore it is electrolytic. Seven-eighths of the current is carried by electrons and is best considered as metallic, particularly in view of the fact that no detectable material effects accompany the passage of the electrons from the solution into or out of the electrode surfaces. The electrodes are completely reversible with respect to electrons.

As concentration is increased, the conductance of sodium falls off much as it does for ordinary salts. For example, the conductance ratio $\Lambda_{0.01}/\Lambda_0$ for sodium is 0.59; for sodium bromide, it is 0.51. In the case of sodium bromide the conductance decrease is due, in part, to the ion-atmosphere effect, but in larger measure it is due to the formation of ion-pairs. The dissociation constant of the ion-pair equilibrium for sodium bromide is 2.9×10^{-3}.

The question arises: Does ion-pair formation occur in metal solutions or do the solutions consist of only sodium ions and electrons? If the best data we have are analyzed by the Shedlovsky method, the computed quantities lie on a straight line from the slope of which we obtain a value of 0.05 for the constant of the ion-pair equilibrium and a value of 1020 for Λ_0. The average deviation of seven points in the concentration range 5×10^{-5} N to 2.7×10^{-3} N is 0.3 per cent. The conductance of sodium in ammonia conforms to the requirements of an ion-pair equilibrium.

The conductance of cesium and potassium in methylamine is much lower than it is in ammonia and the conductance falls off more sharply with increasing concentration. The conductance of cesium at the minimum is only one-tenth that of potassium in ammonia at the minimum. The data in methylamine are somewhat fragmentary, but so far as they go they are consistent with the view that ion association occurs.

When an electron interacts with a positive metal ion the resulting ion-pair is not to be looked upon as a metal atom. In all likelihood the electron interacts with ammonia molecules of the solvated ion much as it does with free ammonia molecules.

The temperature coefficients of metal solutions lend no support to the view that ion-pairs are formed. The conductance of ordinary salt solutions increases with temperatures up to about 25°C.; thereafter the conductance decreases. This decrease is due to a shift of the ion–ion-pair equilibrium toward greater association with increasing temperature. In contrast, the differential resistance-temperature coefficient of a dilute sodium solution is equal to 1.87%/deg. and is constant between $-33°$ and $+85°$C. It should be noted that the temperature coefficients of metals in ammonia are in all cases much greater than the viscosity-temperature coefficient of the solvent which is 1.1%/deg. Temperature increases the conductance of electrons in ammonia in some way other than that of decreasing the viscosity of the solutions.

The picture of dilute metal solutions as outlined above, while still somewhat crude, is probably not too greatly in error. What happens to the electrons in the more concentrated regions in the neighborhood of one normal and above, remains an unsolved problem.

The foregoing summary of the properties of metal solutions is admittedly far from complete. It is hoped, however, that it may serve to stimulate interest in an important field which, up to now, has received all too little attention.

EPILOGUE

In the words of Charlie Chan: "There is a time to fish and a time to dry the nets." With this number, we bring this series of articles to a conclusion. It is hoped that those who have taken the time to read them will have found them interesting if not instructive. A completed investigation is of little interest and, in the development of pure science, it is unimportant. The important things in science are those which are (or seemingly are) *just around the corner*.

ON THE NAMING OF NAMES[1]

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ANYONE who does much research in the history of chemistry, especially in those branches that have descended from sources common to biology, medicine, and pharmacy, must soon become conscious of considerable confusion in the names of many prominent figures. Few names from the earliest times escape altogether, but the most baffling or annoying are those of more or less prominent figures in the alchemical and iatro-chemical periods. By the latter part of the sevententh century, when patronymics were generally established in Europe, the confusion was somewhat resolved.

Some of the causes of trouble seem to be:

(1) *The use of Latin by early scholars, who Latinized their own names.* Once one becomes conscious of this, there is genuine entertainment to be found in trying to ferret out the identity and significance of various *noms de plume.* For example:

Georgius Agricola—Landmann (Bauer?)
Josephus Quercetanus—du Chêne
Andreas Libavius—Libau
Otto Tachenius—Tacken
Robertus de Fluctibus—Fludd
Guilielmus Carnificis—Boucher (Bouchier)
Franciscus Sylvius—du Bois (also de le Boë)
Bertholdus Niger—Berthold der Schwarz
Conradus de Monte Puellarum—von Maidenburg (Meydenberg)
Aegidius Carboliensis—Gilles de Corbeil
Dionysius Zaccharias—Denis Zecaire
Vincentius Bellovacensis—Vincent de Beauvais

A few leaned toward Greek, and appeared as:

Plocotomos—Breitschneider
Trocheoneos—Küffner
Melanchthon—Schwarzerde
Aecolampadios—Hausschein
Xylander—Holzmann
Lycobos—Wolfgang

(2) *Arbitrary transliteration into so-called Roman type, of names originally in Arabic, Greek, Hebrew, and other languages.* There seems to be no good reason for changing the characteristic ending of Greek masculine names *-os* to the corresponding Latin ending *-us*, yet it has been done repeatedly with the names of Aëtios (of Amida), Theophrastos of Eresos, Paulos of Aegina, Oribasios, Synesios, Pedanios Dioskorides, Olympiodoros, and many others.

The lack of vowels in Arabic, Persian, and Hebrew has led to some variable interpretation of the dots used to indicate them. Consequently there is variation in the spelling of many familiar names and of such components as Ebid for Abd, Ebn for Ibn, and El for Al. There is similar confusion in the transliteration of Chinese and Japanese ideographs.

(3) *A nationalistic tendency of later writers to translate into their own language the names as well as the texts of early authors.* This practice seems to be a lack of international courtesy, not to say an impertinence, which is surpassed only by the practice of translating the names of places on maps. The names of Platon and Aristoteles have been "Englished" as *Plato* and *Aristotle* for so long that no one would think of reverting to the original Greek forms. And whoever thought of the nicknames, *Pliny* and *Livy*, for Gaius Plinius Secundus and Titus Livius, respectively, seems to have so labeled them for all time.

French translators (*1*, *3*) tend to soften everything, and Germans (*4*, *5*) lop off final syllables abruptly. Both practices leave recognizable names; but they seem so unnecessary. Old Seneca, for example, becomes *Sénèque* in French; and one finds also *Aristote*, *Herodote Hippocrate*, *Themiste*, *Galien*, *Celse*, and *Jean de Roquetaillade* (de Rupescissa). Even Basil Valentine is anagrammed into *Basile Valentin.* The Germans give us *Herodot*, *Demokrit*, *Theophrast*, and *Olympiodor*, although the Latin (occasionally Greek) ending is kept for certain other names. They drop the *n* for both Bacons—Roger and Francis—(taking it for *baco*, *baconis*, maybe?). Such designations as *Baco von Verulam*, *Thomas von Aquino*, and *Vinzenz von Beauvais* do not seem to be improvements over the original forms.

Some other choice examples are *Wimandus de Ruffo Clipeo* (literally the Italian for Rothschild); *Guillaume d'Avisonne*, for a Scotsman, William Davisson; *Aldobrandino*, for the English Hildebrand; and conversely, the euphonious *Bevelacqua* (Italian), via *Boileau* (French), into *Drinkwater.*

Sarton (*6*) deplores all this translating of names, in the justifiable belief that a man's name should identify his origin, not obscure it. Accordingly, he dislikes the accepted European names for Muslims, and after giving them once for identification, refers to all these writers by their Arabic, Persian, or other original names. The three most famous ones, for instance, are called *ibn Sina* (Avicenna), *ibn Zuhr* (Avenzoar), and *ibn Rushd* (Averroes), these being the nearest to a family name in the (usually discouraging) polysyllabic descriptive designation of each. The same authority also prefers Jewish names, characterized by *ben*, rather than Latinized or Greekish forms; *e. g.*, Moses *ben Maimon* rather than Maimonides.

(4) *Limited knowledge of foreign languages, whereby*

[1] Presented at the 116th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1949.

researchers, not recognizing various forms of the same name, have listed the same person as different individuals. The names thus confused are not always those of lesser individuals. Albert the Great, for example, may be found as *Albertus Magnus, Albertus, Teutonicus, Albert von Bollstädt, Alberto de Collonna, Albertus Grotus,* and *Albertus Ratisbonénsis.* Likewise, in the English translation of a French work, Paul(os) of Aegina was indexed as *Aegynète, Paul, Egine, Paul d',* and *Paul d'Egine.* Other names were similarly confused here, the error, in many instances, having been made in tbe original French book. The Majorcan, Ramon Llull, appears here and there as *Raimundus Lullus* or *Lullius, Raymond Lully, Ramon Lull;* Geber may be *Jabir* or *Djabar;* other examples abound.

Searchers not versed in foreign languages or geography frequently designate individuals by their place of origin, as if it were a family name, not knowing that the man had only one name. Common examples of this are *Guy* de Chauliac, *Henri* de Mondeville, *Bernard* de Trèves (confused with *Bernardo* da Treviso), *Guido* da Verona; and a well-known *Hieronimus* (or Jerome), whose town appears as *Brunswick, Braunschweig, Brunschvig,* or *Brunsschwick.*

Family names are of comparatively recent origin. In the days when feudal lords could be readily identified by the names of their estates and the quartering of their arms, their dependents were usually known only by their given names, and identified otherwise by their occupation (*e. g., tailor, gardener, miller*); or by some physical characteristic (*e. g., bald, bow-legged, squint-eyed, hump-backed*). Later many of these supplementary designations were adopted as permanent family names and patronymics.

(It should not be too difficult a problem of this kind to ascertain which progenitor of that family so famous in chemical industry was the first to be identified by his residence at—or other association with—*the bridge of Nemours.*)

One of the best examples of utter confusion in a well-known name is that of the famous iatro-chemist, Paracelsus. His full name, as given in most texts (including annotated publications of his own works) was *Aureolus Philippus Theophrastus Bombast(us) von* (or *ab*) *Hohenheim.* He adopted the Paracelsus. All possible misspellings of these various names have been found, and the most ingenious explanations of the man's name. His father's surname was Bombast; yet the title page of one book (*2*) presents "The Life of Philippus Theophrastus, Bombast of Hohenheim, Known by the Name Of Paracelsus." In other sources it has been implied that the word *bombastic* was derived from the name of Paracelsus; and that *Paracelsus,* itself, is the Latin for Hohenheim.

Many errors are made by careless researchers who do not notice a difference in dates for two men of similar names; *e. g.,* (Aurelius Cornelius) Celsus (7 B.C.–A.D. 53) and a Celsos (Kelsos) of late in the second century. Crito, an ancient Egyptian physician, may be confused with another Crito who was the physician of the Roman Emperor Trajan (A.D. 98–117). Albertus Magnus (1193–1280) has been mistaken for Albert of Saxony (1316–90); Berthollet (1748–1822) has been confused with Berthelot (1827–1907).

Hoefer (*3*) and Kopp (*4*) have made many references to some of the odd, translated, and otherwise distorted, names mentioned here, and several others. Sarton (*6*) gives all ascertainable variants and aliases of every writer and other notables listed. All Greek names are given in the original, which places accents correctly, but all Arabic, Chinese, Indian, and other characters have been transliterated into Roman type. Unfortunately, this monumental work of reference takes us only through the fourteenth century. In addition to all these earlier languages, a major current source of confusion is Russian.

There should be some one best way to designate these early figures in the history of chemistry. The most logical would seem to be to keep the name in the language of its origin. Long usage however, would probably make it practically impossible to convert older researchers to any names but those to which they have become accustomed.

If any project of reform of this kind is worth doing, how can it best be done?

It is suggested that a committee be appointed from the three Divisions of the American Chemical Society—Chemical Education, Chemical Literature, and History of Chemistry—that may be expected to benefit most from such a study. Possibly the findings could be published in a handy form similar to that of the official lists of abbreviations and nomenclature of chemical compounds. Then, if all we writing chemists could be induced to consult such a handbook faithfully, we might gradually familiarize future generations, at least, with the correct identity of many illustrious figures in the historical background of this science in which we all are interested.

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(2) Hartmann, F., "The Life of . . . Paracelsus," Redway, London, 1887.
(3) Hoefer, F., "Histoire de la Chimie," Didot, Paris, 1869.
(4) Kopp, H., "Geschichte der Chemie," Vieweg, Braunschweig, 1843–47.
(5) Meyer, E., "A History of Chemistry" (translated by George McGowan), Macmillan, London, 1891.
(6) Sarton, G., "Introduction to the History of Science," Williams and Wilkins, Baltimore, Vol. I, 1927; Vol. II, 1931; Vol. III, 1947–8.

A COURSE IN INORGANIC PREPARATIONS

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THIS suggested senior-year course in preparative inorganic chemistry is the outgrowth of a series of lectures and laboratory experiments conducted during the past several years at Wayne University by the authors. The sixteen-week course consists of one or two fifty-minute lectures and eight laboratory hours per week, which present to senior college and first-year graduate students a brief but comprehensive introduction to the aspects of preparative and theoretical inorganic chemistry. The work is designed to meet the requirements of not only inorganic students, but also those interested in organic chemistry and other fields.

The students entering this course are assumed to have had freshman chemistry and qualitative and quantitative analysis. We also assume that they have had or are taking an intermediate inorganic course and thereby having a thorough review of principles. The lectures of the preparative course then are slanted to supplement the intermediate course. We find that this review course is necessary since seniors seem to retain very little inorganic descriptive knowledge from their general or qualitative chemistry.

The lectures are arranged chronologically and are intended to round out the student's understanding of the laboratory work. An outline of weekly lecture topics follows. Certain necessary laboratory techniques are discussed in the first two weeks, enabling the student to begin laboratory work. Among the topics discussed are safety, handling of dangerous chemicals, techniques in crystallization, sublimation, distillation, filtration, drying, and solubility. The lectures on purification procedures are exemplified in the laboratory by such assignments as rock salt, mercury purification, etc.

Outside reading for these lectures is suggested in the following texts:

HAROLD F. WALTON, "Inorganic Preparations," Prentice-Hall, 1948.
WM. E. HENDERSON AND W. CONARD FERNELIUS, "Inorganic Preparations," McGraw-Hill, 1938.
HEINRICH AND WILHELM BILTZ, WM. T. HALL, AND ARTHUR A. BLANCHARD, "Laboratory Methods of Inorganic Chemistry," John Wiley, 1928.
EBENEZER H. BLANCHARD AND JOSEPH W. PHELAN, "Synthetic Inorganic Chemistry," John Wiley, 1922.
ALEXANDER KING, "Inorganic Preparations," D. Van Nostrand, 1936.
EBEN HENRY ARCHIBALD, "Preparation of Pure Inorganic Substances," John Wiley, 1932.
JOEL HENRY HILDEBRAND, "Solubility," A. C. S. Monograph, 2nd ed., Reinhold, 1936.

The lectures during the third and fourth week are devoted to the use and handling of laboratory apparatus such as ovens, furnaces, vacuum pumps, pH meters, microscopes, refractometers, etc. There is need for the student to be able to use the more common laboratory instruments correctly. We have found our students' previous experience, in the use of the above apparatus, inadequate or even nonexistent. Some of the laboratory preparations are chosen for their value in demonstrating the need for a chemist to construct his own tools and apparatus. Simple techniques in glass-blowing manipulations are taken up and demonstrated. A student, we feel, should be able to construct simple pieces of glass apparatus and make a small vacuum line for handling certain gases.

Suggested reading is in the following texts:

FRANCES COWLES FRARY, CYRIL S. TAYLOR, AND JUNIUS D. EDWARDS, "Laboratory Glass Blowing," McGraw-Hill, 1928.
THOMAS P. CARNEY, "Laboratory Fractional Distillation," Macmillan, 1949.
HOBART HURD WILLARD, LYNNE L. MERRITT, AND JOHN A. DEAN, "Instrumental Methods of Analysis," D. Van Nostrand, 1948.
DAVID F. BOLTZ, "Modern Instrumental Analysis," Edwards Bros., 1949.

The fifth-week lecture is devoted to the newer ideas of nomenclature, the student having by this time run up against the problem of correctly naming his preparations. The student's elementary concept of the subject is reviewed and expanded to include recent ideas on the naming of complexes.

The following articles are recommended:

W. P. JORISSEN, H. BASSETT, A. DAMIENS, F. FICHTER, AND H. REMY, "I.U.C. report—1940," *J. Am. Chem. Soc.*, **63**, 889 (1941).
W. CONARD FERNELIUS, EDWIN M. LARSEN, LOUIS E. MARCHI, AND CARL L. ROLLINSON, *Chem. & Eng. News*, **26**, 520 (1948).
W. CONARD FERNELIUS, *ibid.*, **26**, 161–163 (1946).
JANET D. SCOTT, *Chem. Reviews*, **32**, 73–96 (1943).
JANET D. SCOTT, *Chem. Abstracts*, **39**, 5869 (1945).
ATHERTON SEIDELL, "Limitations upon the unification of chemical nomenclature," J. CHEM. EDUC., **6**, 720 (1929).
GERALD R. BEEZER, "Latin and Greek roots in chemical terminology," *ibid.*, **17**, 63 (1940).
MARY ALICE EWING, "What's in a name," *ibid.*, **15**, 123 (1938).
W. P. JORISSEN, H. BASSETT, A. DAMIENS, F. FICHTER, AND H. REMY, "Rules for naming inorganic compounds," *J. Am. Chem. Soc.*, **63**, 889 (1941).
GEORGE W. WATT, "The designation of special isotopes in the names and formulas of inorganic compounds," *Science*, **108**, 2818 (December 31, 1948).

The sixth and seventh lectures are devoted to phase rule theory and its application in the separation of salts and the stabilization of salt hydrates. Use and interpretation of diagrams is illustrated on the blackboard.

Outside reading is suggested in the usual physical chemistry texts, also:

ALEXANDER FINDLAY, "The Phase Rule," Longmans, 1938.

By the middle of the semester some assignments are made from original sources; one object of the course being to parallel research procedures as much as possible; hence, the eighth lecture is devoted to library methods. Students are asked to use library references to obtain preparation procedures from the original workers. In some cases the formula is assigned, in others the name is given. A working knowledge of library methods and systems is needed by the student; therefore, a briefing lecture on literature surveys is important. Not only does this type of assignment afford the students the opportunity to obtain practice in the uses of the library, but it also permits them to utilize their knowledge of foreign languages. Students, we find, develop respect for their work if the "cookbook" procedure is minimized.

References:

BYRON A. SOULE, "Library Guide for the Chemist," McGraw-Hill, 1938.

EVAN JOY CRANE AND AUSTIN M. PATTERSON, "A Guide to the Literature of Chemistry," John Wiley, 1927.

MELVIN GUY MELLON, "Chemical Publications," McGraw-Hill, 1940.

The latter part of the series of lectures is devoted to the theoretical concepts of inorganic chemistry, enabling the student to understand the chemistry of the compounds prepared in the laboratory. The ninth-week lectures, occurring after a midsemester test, are a review of the periodic system. Use of the periodic system in predicting chemical reactions is emphasized. The tenth-week lectures are devoted to oxidation-reduction potentials and a review of what prediction can be made therefrom. The eleventh-week lecture material reviews valence and the relation of bond orbitals to valence. The twelfth- and thirteenth-week lectures are used to discuss complex compounds. The following subjects are taken up: role of central atom, coordinating groups, stability, general properties, types of isomerism. The last two lectures are devoted to discussion of the structure and means of evaluating the structure of compounds.

The following books and articles are suggested outside reading during the second part of the course.

Harold F. Walton	"Inorganic Preparations"
Wm. E. Henderson and W. Conard Fernelius	"Inorganic Preparations"
Harold Simmons Booth	"Inorganic Synthesis," Vol. I
W. Conard Fernelius	"Inorganic Synthesis," Vol. II
Ludwig Frederick Audrieth	"Inorganic Synthesis," Vol. III
James Riddick Partington (Macmillan, 1950)	"Text-Book of Inorganic Chemistry"
Wendell M. Latimer and Joel H. Hildebrand (Macmillan, 1947)	"Principles of Chemistry"
N. V. Sidgwick (Oxford Press, 1951)	"The Electronic Theory of Valence"
G. N. Lewis (Chem. Catalog Co., 1923)	"Valence and Structure of the Atom"
N. V. Sidgwick (Cornell Press, 1933)	"The Covalent Link in Chemistry"
Edward Bradford Maxted (Oxford Press, 1947)	"Modern Advances in Inorganic Chemistry"
Wm. George Palmer (Cambridge Press, 1948)	"Valency"
Alexander Frank Wells (Oxford Press, 1947)	"Structural Inorganic Chemistry"
Wm. Thomas (Blackie & Son, 1924)	"Complex Salts"
Robert Schwarz (Wiley, 1923)	"The Chemistry of Inorganic Complex Compounds—An Introduction to Werner's Coordination Theory"
H. J. Emeleus and J. S. Anderson (Van Nostrand, 1947)	"Modern Aspects of Inorganic Chemistry"
Wendell M. Latimer (Prentice-Hall, 1938)	"Oxidation Potentials"
N. V. Sidgwick (Oxford and Clarendon Press, 1950)	"Elements and Their Compounds"

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K_2CS_3 and $BaCS_3$
K_2CrO_3
$Co(NH_3)_4CO_3NO_3 \cdot {}^1/_2H_2O$
Lead Tetraphenyl
$Pb(NO_3)_2Pb(OH)_2$
CuCl
$Sb_2(SO_4)_3$

The following are taken from "Inorganic Preparations" by Harold F. Walton, Prentice-Hall.

Hydroxylamine Hydrochloride
NaCl Reerys.
$MgCl_2$ Anhyd.
Sulfamic Acid, SO_2NH_2OH
$Ti(SO_4)_2$ Soln.

Examples of preparations taken from "Inorganic Syntheses," Vols. I and II.

Potassium Trioxalatocobaltiate $K_3(Co(C_2O_4)_3)3H_2O$
Hydrazine Sulfate $N_2H_4 \cdot H_2SO_4$
Bromopentammino-Cobalti Bromide
Iodine Trichloride
Fe(II) Bipyridyl Perchlorate
$NiN(CH_2—NH_2)_2(SCN)_2$
$(NH_4)_3SbBr_6$
$Ba(SCN)_2$
H_2NCN Cyanamide
Potassium Azide

The preparative part of the course is arranged to give a wide coverage of various types of compounds and to cover as many of the elements as possible. Except at the start of the semester's work, no attempt is made to arrange the preparations as to difficulty, but emphasis is placed rather upon giving as representative a covering as possible. The preparations selected are those which we have found correctly described in the literature. Several hundred preparations have been evaluated by our students during the past few years. Assignments are made mostly from a card index file, although some are taken from the several standard inorganic preparations manuals. Many of the assignments are made by giving the student only the correct name or formula of the compound, the journal or the book reference not necessarily being stated. A number of standard texts are placed on reserve in the library or are left in the laboratory. The student is thus on his own, except that he must do his preparative work during the regular laboratory hours. No two students are given the same assignment during a semester. Upon completion of a preparation, the student submits a specimen in an appropriate container, properly labeled. For each student enrolled in the course the instructor has a record card showing the student's preparation assignment. Care is taken that not more than two or three preparations are assigned in advance and that the student does not spread his time too thinly.

We feel that a balance between descriptive inorganic chemistry and the theory pertaining thereto is most desirable. Uncorrelated facts are not well retained by students, regardless of how important they might be. As the boundaries between inorganic and organic chemistry gradually disappear, it is felt that the lecture as well as the laboratory part of the course must take this into account. Thus we find it is good practice to draw upon the numerous borderline examples of organic chemistry as exemplified in the complex inorganic compounds having coordinated organic groups.

The laboratory part of the course must present ample opportunity to the student to acquaint himself with the analytical, organic, and physicochemical methods that

are the required tools of research. Therefore, we ask our students to prepare and characterize some of the Werner complexes and some molecular-addition complexes in addition to the more common inorganic compounds. The student should also acquire a fair knowledge of the preparation and purification of organic intermediates used in inorganic preparation. Often other members of the department are in need of a certain inorganic chemical not readily available. In such cases a student is asked to prepare larger quantities than usual. We find students develop more interest and pride in their preparation if it serves a useful purpose.

A typical set of assignments is the following:

1. Sodium chloride purification. Rock salt is the starting material. The students are referred to "Inorganic Preparations" by Harold F. Walton or to "Inorganic Preparations" by Wm. E. Henderson and W. Conard Fernelius. All students do this as their first preparation.
2. Preparation of $KMnO_4$. } The above references are used.
3. Preparation of HBr. }
4. Preparation of $SnCl_4$. Beginning with tin metal and chlorine gas. The gas is either supplied in a tank or the student could be asked to prepare his own. The product $SnCl_4$ is distilled.
5. Preparation of anhydrous $MgCl_2$. This preparation gives the student experience in working with hygroscopic substances.
6. $Cu(NH_3)_4(NO_3)_2$. The student is given the following reference: *J. Chem. Soc.*, **21**, 2636 (1922).
7. $C_5H_5N\text{-}SO_3$. "Inorganic Synthesis," **1946**, Vol. II, pp. 173–4.
8. Preparation of Karl Fischer Reagent. Student makes his own literature search.
9. Preparation of Cobalt (III) chloride. Literature reference: *J. Am. Chem. Soc.*, **60**, 3053 (1938).
10. BF_3. Literature must be examined.
11. Aluminum acetylacetonate, $Al(C_5H_7O_2)_3$.
12. $Ba(AlO_2)_2$. Student makes his own literature search.

The students keep a research-style bound working notebook in which is entered the library search details, the pertinent observations made during the preparation, the yield obtained, and the procedure used.

All compounds submitted for approval to the instructor are accompanied by a detailed report which includes a description of the procedure, theory involved, material used, yield calculation, and any necessary analytical data. A file is kept for each student's reports.

Individual assignments to each member of the class result in the student finding himself free to rely upon his own judgment and able to express confidence in his own labors. His own development is further enhanced by being permitted to work at his own leisure, without too much restriction of time.

Grades are based on the instructor's evaluation of the student's technique, a midsemester test, a final test, and a term paper discussing the properties of a compound or an advanced inorganic concept.

The authors have found this course plan to be quite popular and to arouse the students' interest to the extent that many have selected this course as one of their electives, even in premedical curricula, where it is not required. The preparation of the more unfamiliar compounds such as the complexes arouses much interest.

Class size during the past several years has varied from fifteen to thirty students, the course being offered twice a year. We have also found that a single period is preferable to two split laboratory periods.

In addition to the usual glassware found in a classroom laboratory, we have found the following items desirable or necessary:

1. Oven
2. Electric muffle furnace
3. Small gas muffle
4. Tube furnace
5. Ice chest
6. Dry ice chest
7. pH meter
8. Vacuum pumps
9. Chemical microscope (polarizing)
10. Steam bath
11. Fractionating column (usually constructed)
12. Glass-blowing torch
13. Centrifuge
14. Ball mill

Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

SCIENCE EDUCATION[1]

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WHEN Austin Kibbee first suggested I prepare a paper for this meeting, I thought it would be rather uncharitable to say "No" to a man paying for a long-distance call out of a school teacher's salary. I had first thought to pick a safe subject, like textile research, about which I knew something, but you, perhaps, very little. Having previously expressed (to Mr. Kibbee's knowledge) some thoughts on education, I then thought I might venture into your field, but giving you the viewpoint of an outsider. I could at least speak as a product of science education, and as an employer and associate of such products in industrial affairs. But as my thoughts progressed I found even that assignment rather cramping. If my thesis is right, science education for industry is no different essentially from science education for anything else. And so I broke down all limitations and have assumed the title for this talk "Science education for anything and everything." If I seem to flounder, please pardon. At least I am having the nerve to bring up things which most others have preferred to dodge. I hope better spokesmen for my thesis will be able to present it more coherently as time goes on.

In pursuing this I am not going to differentiate between mathematics, physics, chemistry, and the biological sciences. If my thesis is correct, these have far more in common than in distinction.

First I shall talk about objectives. Why is science taught in the schools, anyway? If we run through the "why's" now, perhaps we can better view the "how's" and "wherefore's" later. In going through these I will assign no rank or priority. I will skip lightly over the obvious for the sake of devoting time to the more obscure but none the less significant.

Number one, of course, is the need to stretch and diversify the curriculum. Science subjects help keep youth busy with relatively harmless activities during that difficult period when their glands have stolen an extra lap on their senses. One can only go so far and reach so many with the banana countries, Gettysburg, Silas Marner, football, and the socially acceptable French verbs. Some of the others must be diverted by burets, prisms, equations, and frogs.

Let us not underrate this "preventive" phase of education. Beyond its immediate effect on motor fatalities and "good-will" home statistics, it has enduring value as a habit-former. An experience with intellectual hobbies, even though by regimentation, leaves its mark. Who knows but what anarchy itself is staved off by people's preoccupation with reading, tinkering, and arguing of petty details. Science education is particularly important in this because of its retention value. Men boast of their ignorance of Caesar, Proust, and Rand-McNally, but feel a real kinship with both Edison and Einstein.

A second purpose of science education is to help shape the all-round man, and, if not overdone, the nicely rounded woman. This objective is assumed by the hazy but basically sound instinct of the classical traditionalist, and is also claimed by the hard-boiled realist who figures, "you never know what you are going to run into." The all-round person is that because he has perception for, appreciation of, and perspective on, many things. He can judge a man by his speech, attitudes, talent, and vital forces and form a coordinated impression. He can hear a factory whistle and know it as a pulsating column of vapor as well as a shrill summons to servitude. He views a traffic accident and carries away a total memory including kinetics, high-octane fuel, and low-compression brains. In all these he senses the objective as well as the subjective. No one will dispute the place of science education in man's ability to know himself and what goes on around him.

My third item may have been generally overlooked, but it is deserving of attention. It is real and explains in good part the popularity of science courses today, and can thus be considered a justification if not a conscious objective of science education. It has to do with prestige in the battle of the sexes, and in the battle of the generations.

You remember it was Eve who first assumed a taste for the fruit of knowledge. Adam went along with the idea with, I imagine, no great enthusiasm, but prompted

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by the thought, "No mere girl is going to out-dare me." Ever since he has sought fruits of his own finding, to eat first and tease the little woman with occasional nibbles. I suggest that the developments of commerce, militarism, industry, politics, and science owe as much to sex rivalry as to any other motive. Man created a "Man's World" because he felt uncomfortable and at a disadvantage at home. That thought may be worth a book some day, but it is brought in here for its specific application to science education. While the girls exhibit their advanced physical maturity and greater abilities in cultural and social fields, where are the boys? A favored few whose genes have clicked over a little faster are maintaining a status on the field, court, or dance floor. A great number of the more downy lipped, the acne plagued, the falsetto voiced, have bent their knobby knees to science. That's man's stuff. As compared to the girls, these lads can at least hold their own in math, predominate in physics and chemistry, and slice up their specimens without squealing. They take their refuge in technical studies and technical hobbies. Why do male teachers in general have better luck in teaching the sciences? That solid baritone, intoning substantial subjects, is a great comfort to those needing it desperately at that stage of their development.

The same applies to those not scheduled for higher learning. They seek the manual arts by preference. And if perchance their faith in the white collar myth has kept them in cultural, general, and commercial courses, they feel ill at ease and apologetic.

Interesting and serious science education *is* vitally needed to help the boys live with dignity through this period when their sisters have temporarily out-distanced them in so many other factors. As a side remark I observe that the boys are not aware of this consciously, now or later. But don't mistake that the girls haven't figured it out. They learned early in the contest that it is smarter to let the boys look under the hood while they make some silly remark that perhaps the timer needs winding. The lads are so much more chivalrous and tractable thereafter.

Science education can also be a refuge for a minority of girls, those ill-favored few with physical short comings, and those with an excess endowment of brains. If they lack artistic talents to lean on, what better way to make out that fate is choice than to ascribe to science seriously, outwardly scorning the secretly envied frivolity.

Science education has prestige value in the home also. In this jived-up age, with such a difference in succeeding generations' contemporary *milieu*, youth is viewed as might be a Martian invasion. Most of youth's aspirations, if apparent at all, are considered with bafflement or horror. But how Mama beams when Junior first asks her to "Please pass the sodium chloride." That is solid. Maybe the boy will amount to something after all. A mention of Oak Ridge puts parental chins in the air as did references to the cloth or to the bench in previous generations. At least one can always say later that the dear lad had such a brilliant career in science ahead of him before the Draft Board curtailed his further training.

I will now touch briefly on two other objectives of generally unappreciated significance. The first of these is an extension of the prestige principle, though it has economic ramifications as well. It has to do with mastery of the common tools of living. As it is, it is not only a painful financial experience but an act of humble surrender to call in a plumber, electrician, mechanic, or other artisan. They have got us where they want us and are making the most of it. They have installed in our homes and garages things a little too complicated for our Mother-wit to cope with, adroitly imperfect enough to need attention, yet not so complicated but what they themselves by specialized concentration can at least give to amateur eyes an impression of mastery. Our forefathers may have hired craftsmen, but they knew what they wanted done and saw that it was done according to their own ideas and experience. Can you imagine that fierce looking old boy in the daguerreotype being persuaded that he needed a new pump when he himself could cut a new leather valve from an old boot? He had a dignity and respect as head of the household that we sadly lack. I submit that if more fathers could find skipping spark plugs, more sons and daughters would listen respectfully and receptively when being lectured on morals and life.

The second of these insidious trends, for which I claim science education as the sole effective countermeasure, is that our U. S. economy is falling completely into the hands of the sales department. We consumers, who should be the solid base for a democratic economy, can no longer tell plate from sterling, in fact will settle for base metal if intriguingly packaged and extolled between innings. Value and suitability are academic considerations, for guile, bedazzlement, mesmerism, and outright duplicity are the controlling factors. The trash which floods our markets represents a prodigious waste of materials, fuel, labor, ingenuity, and nervous energy. It is getting so that in many lines it is difficult now to find either source or outlet for soundly engineered and factually described products. Commerce has always had its medicine men, but they came to town but once a year. Now they have moved in on both sides of Main Street, and having crowded out everything else, are overflowing to the outskirts of town again, where the sheriff used to keep them. To restore saneness to our economy requires a general cultivation of perception, logic, and judgment, which, as they deal with material things, clearly calls for science education.

We now come to the more obvious objectives, to which I intend no disrespect in mentioning them only briefly. In our minds so strongly now is the matter of military necessity. As related to weapons, one might say that early wars were waged by unskilled labor. World War II brought into predominance the war of mechanics, and later the technicians. Scientists

are supposed to take over from there. (If there is any after that, it may be back to clubs and spears again.) But at the present time it is foolish to dodge the fact that military preparedness and effectiveness depend on the scientific skills of not only the armorer back home but the poor guys up front.

Next is the matter of industry. It is perfectly clear that the middle echelons of our major industries must be staffed with persons of some knowledge of the sciences. The machine would not tick, or in fact be there at all without such people. The practical application of scientific developments, and the day-to-day control, require something more than native talents and rote learning.

We will end up the list of "Why's" with science education for scientists. We have to have a few of these warped souls around to do the exploring, classifying, theorizing, experimenting, and inventing, or life would just be too dull. Most of what they do is commendable. So if you will concede that there should be scientists you will have to accept science education.

Well, I have babbled on at some length now and perhaps it is time for a summary. I have suggested that science education holds justifying significance as related to the following:

1. Keeping youth busy
2. Completing the all-round man
3. Improving morale
4. Restoring the master to the household
5. Restoring democracy to the economy
6. Fitting for warfare
7. Preparation for industry
8. Training scientists

I have chosen to spend some time on these objectives, for without reasonably defined goals there is no basis for discussing methods, efficiency, or accomplishment.

Now the first thing to do in conducting a program of multifold purpose is to concentrate heavily on the factors which are in common to all objectives, and then later to see to it that by specific adaptation each individual case is satisfied. Well, let's follow that course. What are the factors which control success in all these areas?

First and foremost is the cultivation of the art of observation. Common man "Oh's" at the stars and "Ugh's" at the bugs and lets them go at that. The scientist focuses his telescope and microscope, gazes intently, and forms an objective and reproducible impression. Can you point out any in my list of goals for which intelligent and accurate observation is not the major key? It is odd that this is one of the skills hardest to teach, for it is so strong a trait in infancy before being lost to juvenile sophistication. Just as an example I imagine that many of us who could not describe in proper sequence the route from home to office, could still recall a vivid and precise picture of the route from home to kindergarten. The importance of this knack and skill for accurate and objective observation increases with the complexity and speed of civilization. There is so much more to see, therefore less time to view any one scene or situation and have it register. The penalties for inaccurate or incomplete observation are just as severe and even more swift than they were back in our days in the jungle. The fellow who cannot see the woods for the trees is pitied by all. More to be pitied, however, is the average man who is habitually in mid-focus and cannot bring either trees or woods into sharp definition. He knows neither detail nor generality and lives and acts in a haze of blurred assumption. To go back to our analogy, my point is that the forester must first be an arborist, building up his knowledge of the woods as cumulative knowledge of the roots, bark, and leaves.

The powers of observation, as to alertness, speed, and accuracy should be developed in the classroom both by emphasis in every situation and problem, and by direct drilling. In fact the student should be unmercifully hounded into correct habits of observation, until they again are as automatic as the original instinct. It is the starting point for all knowledge, not only for science, but it is a discipline best taught by reference to science subjects, and by the type of teacher one should hope to find in science courses. If you accomplished no more than this, but did that thoroughly, you can know you have served your clients well. You must be aware that the world your students will face 10 and 20 years from now will have new facts and new emphasis. You cannot anticipate on subject matter, but you can prepare your students to look over the new situations with shrewd and practiced eye. They will recognize the familiar, register the new, and be preparing for action while the untrained are still blinking.

The next phase, of course, is the training in ability and habit of making sense of what is seen. We cannot help acquiring some level of this ability just in the *natural* processes of growing up. But nature is trusted far too much. The slow accumulation of such wisdom just through living, unfortunately, seldom reaches a respectable level until an age at which both powers of observation and energy have already been seriously impaired. This skill must be taught by intentional and specifically directed programs, and taught in the years before one is called upon for major decisions and actions.

There are many parts to it, and the problem must be broken down into these elements. Simplest is the understanding of direct phenomena of cause and effect. Much of man's present befuddlement is his inability to solve the riddle of the hen and the egg. Habits of discernment in this relationship are vital, not only in the laboratory but in the home, shop, market, and the very world itself. Training in this, as it is well within your province to give it, will help solve the problems of who started the argument, what monkey wrench first jammed the works, how the panic got started, and whether a high birthrate brings starvation or the other way around.

Getting beyond the simpler relations, there is the training in charting the tangled web of multiple systems with their interactions and various degrees of freedom. If taught solely as incidental to acquiring technical concepts, it is a poor thing indeed compared to its potential value. If taught as a recognized art, it loses none of its value in scientific matters and is applicable to all human affairs. It would go far in clearing the bewilderment and frustrations of spouse, parent, citizen, and administrator.

A third matter of training is in appreciation of qualitative factors and the methods of identification. In chemistry in particular we specialize in relating substance to behavior and capitalize on the specific qualities of the elements. We learn to expect A to behave like B in some reactions, but through some subtle difference in its internal make-up to follow a different course in other circumstances. Why not ground the student with a general background in qualitative analysis, and follow up the chemical details later. His training would be equally applicable to psychological and social problems. Without such deliberately developed attunement of the discriminatory senses we make the dual mistake of over-generalizing on the one hand and failing to note similarities on the other, and these mistakes plague us through all our affairs.

A fourth segment of this general phase of training is development of acuteness and astuteness in quantitative affairs. One should start right with the theory of unity, numbers, measurement, and analogy, and carry right through to the physical basis for exponential powers, functional relationship, and statistical concepts. Then later get down to the tricks of calculations and estimations. One of the most tragic wastes in education today is the abstract and sterile nature of mathematics teaching both in the formal courses and as used in the other sciences. Math could have such significance! It could provide a basic tool for understanding all the quantitative factors of life. Proof that it is failing its potential is in its distinction of having the lowest retention rate. But there are quantitative aspects in all affairs, both mental and physical. The habits of recognizing the significance, proportionalities, and calculable relationship of things are essential to perspective and understanding in any field, and should be cultivated with all due emphasis and diligence.

These four aspects, and others we have not mentioned, of what we might call the interpretative phase of science education, must then be combined into the master skill of coordinated perception. I said first that to begin the training we must give each separate factor recognition and attention, but even from the start each must be directed towards the ultimate merger and then put through joint maneuvers. The result is a balanced perspective, a consummation devoutly to be wished for.

The third major common objective of science education is development of the habit of doing something with the knowledge acquired in the first two. This poses a problem for some educators, for creativeness cannot be taught by those who have never created. This calls for both example and inspiration.

The student in his formative years must be provided ample opportunities for the total experience of sizing up a situation, surveying the material, formulating a method, mustering his tools, conducting the work, and evaluating the result. This of course is the premise on which the so-called "progressive" schools are based. Their contribution to the philosophy of education, however, may be greater than that to their students. In emphasizing this third objective they have overlooked the importance of the two preliminaries.

In graduate work the project method is of course traditional. But that experience is only for the select and comes far too late in life. Being a first experience, little may come of it either to the benefit of the scholar or his sponsorship.

Part of this third major phase is in techniques, and part is the starting, long before the threshold age of 40, a progressive chain in which one success is the key to the next. For the methods, I list first the habit of anticipation. A good skull-scratching early will save many a headache later. Forethought is a habit which comes only with training. Lack of it dooms many projects to failure from the start.

Efficiency is a developed talent, and one which science education should stress as a basic technique of successful accomplishment. The principles of purposefulness, conciseness, and definitiveness are teachable. Life is too short to ignore them.

Another technique is in making best use of secondhand knowledge. There should be real training in consulting the references, testing for reliability, assessing the pertinency, and applying to the problem. The student should be guided as to both the values and pitfalls of analogy. He should develop a conscious working balance between faith and suspicion in utilizing the recorded knowledge.

Another is the habit of cumulative experience. He should learn the habit of continual review of his conclusions in the light of current facts, experiences, and thought organization.

The student should learn how to make proper records, interpret and summarize, and transmit knowledge. He should learn early in the game the dangers of unfounded conclusion and of ambiguity of expression.

These are the things that count in science education. The rest is incidental. My word to you is, "Teach the methods and let the subject matter fall where it may." I know you have to pay some respects to prescribed procedures and fact-jamming standards. But in the privacy of your classrooms you have far more latitude than you have ever dared use. To get down to cases, I'll bet you the price of a slide glass that if you ever once had courage to leave the textbooks on the shelves for the first two months of any year's science course, and devoted that time to a preview of

the course, the history of that field, its key principles, and its relation to other fields, and in drilling the class by demonstration, games, and problems in the abilities for observation, coordination, and perspective, and original accomplishment—you could breeze comfortably through the textbook and bench assignments in the remaining time with ample opportunity for a summary and celebration at the end. I know that class would not only know something; they would know why they knew it, how to know more, what might be done with the knowledge, and what to forget after exams. That class would chip in most heavily on your retirement gift, and have the biggest bouquet at your funeral.

Let's be realistic. What percentage of the subject matter will be remembered anyway, and if remembered be put to any satisfying use? It's a real percentage, but almost so small as to be considered in the special case category. There are certain parts of all courses which will relate to the careers or lives of most of the students. There are certain students whose obvious talents or aspirations single them out for individual detailed cramming. As it is, we strike an average class level of emphasis which fits no one. It is like figuring that the center of population for Western Civilization is somewhere in the watery waste of the Atlantic Ocean. Those whose sole practical need for a science education is on the level of computing their income tax, fixing the doorbell, or explaining to Susie why the goldfish died, do not even retain that much, because those matters are indiscriminately shuffled in with matters of no later direct personal concern, and forgotten accordingly. Those who may later be involved in technological affairs do not get grounding in the relationships of things, and find it difficult later, on their own, to associate their schooling with their careers. Those who intend real careers in science still lack the training in scientific methodology, and have acquired subject matter over hours of memory study which they later might have picked up in ten minutes if they needed it.

It wasn't so many years ago that a science graduate was an expert whose schooling in factual knowledge put at his command ready answers to the questions which would be put to him. Speaking particularly from the viewpoint of an industrial researcher, I want to impress on you that the questions at that level have all been answered. The questions of today are either too intensively specialized for any school to touch on, or too extensive for a junior to be able to even comprehend, let alone cope with. Yet you have only about the same type of human material to work with, and the same number of semesters to work in. Let's just stop pretending that the schools are going to turn out chemists, physicists, and the like in the sense of a generation ago. And for heaven's sake knock that illusion out of the kids' heads and their parents' too. If they are going to be anything at all *now* in science, engineering, advanced industrial technology, or biology and so forth, they have a lot higher yet to go in graduate studies and specialized on-the-job experience before they can begin to make any real contribution. But the higher one is to go, the broader and sounder the base must be. I say that sounder base is in the *general* habits of seeing, thinking, and working along the lines I have suggested.

In the opposite direction, if the vehicle isn't to get off the ground at all, build something substantial and competent for the terrain it will cover and do not try to load it down with all the instruments for celestial navigation.

To sum this up, the three skills of analysis, coordination, and positive accomplishment should be the objectives of all science courses no matter what the subject and no matter who the student. Facts, figures, and applied techniques will be absorbed by the process of association. This absorption will be found to be almost automatically adjusted both qualitatively and quantitatively to the abilities and aspirations of the students, and what is not self-adjusting can be compensated for by a small amount of individual coaching. It is better to have all students able to work a few simple problems from first principles than try to arm them with a quiver full of derived theorems and equations.

Now why do I think this is so almighty important? Why am I hammering at you? You are no more to be criticized than the rest of the educational profession, being only human, and yourselves products of an imperfect education for which you were not responsible. The products of your teaching "get by" according to general standards of this imperfect world. The public is getting the usual value for what it seems willing to pay for or ask for.

I wish I had the powerfully inspiring oratory of the evangelist to wind up this talk. Lacking that, I plead with you to try to understand the message for which I have so far only tried to alert you.

Do you really know your place in history? Do you realize that you science educators are at the apex of the two great trends of civilization and human progress? What happens from here on is in your province of control. Do you even dimly sense that in your hands rests the fate of the world?

First, on you as educators rests the responsibility to vindicate that grand assumption that the broad base of native and developed intelligence is of a high enough order to guide by its mass action the common welfare, and do it better than is liable to be done consistently by arbitrary authority. Democratic social organization was first ventured in the day when native wit and instinct were reasonably adequate to judge the current issues. But as in science, so in political and economic life, the world's affairs have long since gone far beyond that level of complexity. A much higher level of intelligence is called for to maintain balance, control, and progress. That means development by formal education. That means you. The home and family produce in succeeding generations too small an increment of increasing intelligence to keep up with our rapidly accelerating need. Only

professional educating specialists can do the job. They cannot do it unless they realize that mission in all its implications, accept it as their guiding motive, and give it the best they have. To pass on only what you now know means that the lag of intelligence behind circumstance gets longer and longer, and it is a dangerously long lag now. But if you can teach the purposes and significance of knowledge and the methods of acquiring and exploiting it, you will be building responsible and solid citizens who can keep up with their times. That is a statement true for all branches of education.

As science teachers, however, you hold the key not only to the mechanisms of life, but to the very philosophy of life. That statement will probably shock you, for science has made almost a fetish of avoiding any dealings with values, ethics, and the great human verities. You were supposed to work on mechanisms and let somebody else worry about purposes and uses.

Science has been the main instrument, however, in challenging and discounting the authority of the old standbys, the faiths and codes by which earlier civilization was ordered. It behooves science to offer something more reliable, and at the same time more dynamic and adaptable in their place. In your generation and in your profession we find the merger of these two great movements: the broadening of the base from which authority is derived, and the prior reliance on rational logic over assumptions and tradition in controlling thought and action.

The recognition of this crisis in our destiny and the right application of emphasis in your teaching are vital to the combined success of this merger. The methods of science, as applied to the greater references of life and civilization, are more important than further advances in science itself. We would be better off at this point to freeze scientific and technological factual knowledge at its present level, if by so doing we could divert the skills and energies of those normally engaged in such activities to the broadening of mass intelligence.

How else will the public ever measure up to the responsibilities it has assumed? Where else will citizens acquire the skills of observation, perspective, and accomplishment? Who else will orient the thinking of common man to comprehend the fluid and dynamic forces which affect their lives? Who else will teach the habits of discrimination? How else will man acquire the knack of acting on cumulative experience, so that his working hypotheses are current on any day and intelligently modified with the experiences of tomorrow?

These things are the basic laws of rational living, both in the sense of the individual and of the group. They are far more important than any detailed subject matter you can submit. *And*, there is no other mechanism for teaching these principles and methods than the science educator.

The old temples are crumbling down. The palaces are now museums. The forum is now a burlesque hall, the art shrine in the hands of the concessioneer, and the board room given over to the advertising department. The cloistered courts of learning are now curb-service snack bars for indigestible specialties. The old institutions have lost their authority by default, folly, and general inadequacy. Most important, they never were built on a broad enough base of general human experience.

Science has provided wonderful materials and ingenious tricks for assembly of a new edifice. It can build as high as man aspires, and as broad as mankind needs. It can provide for expansion and adaptation. It can build in inspirational beauty, and at the same time complete functionality.

I warn you, it will be the last temple ever built by mankind. If it is built on inadequate foundation, in fact on anything less than broad and deep mass support, it will never get very high or be very stable. If jerry-built, it will come tumbling down and carry humanity with it in the most tragic disaster of all. The pieces will serve then only for props for underground shelters in which the remnants of mankind will huddle until celestial fate overtakes them. This is it, folks. This is the last chance. We'd better give some thought to the blueprints.

To the Editor:

A letter in the November, 1952, issue by J. S. Miller, asks how one can predict the upper limit of swelling of rubber gloves in a solvent. There can be no exact answer to this question since the degree of swelling of vulcanized rubber varies from one sample of rubber to another.

Among the numerous factors affecting swelling are the per cent combined sulfur; the vulcanization accelerators and antioxidants; compounding ingredients such as carbon black, zinc oxide, and plasticizers; the degree of oxidation of the rubber hydrocarbon before, during, and after the manufacturing process; etc, etc.

From the data given by Dr. Miller, I would hazard a

prediction that in a few months time whatever antioxident the gloves originally contained would have been leached out, oxidation would have reduced the molecular weight of the rubber hydrocarbon, and the rubber would have gone into colloidal solution.

PHILIP L. BRUCE

LONG BEACH, CALIFORNIA

To the Editor:

During the concluding session of the Conference of College Chemistry Teachers, held Friday and Saturday, November 14 and 15, on the Monmouth College campus, 90 representatives from 53 liberal arts colleges joined in the formation of a regional chemistry teachers association. The new group will be known as the Midwestern Association of Liberal Arts College Chemistry Teachers. Dr. Harry Lewis, Dean of The Institute of Paper Chemistry, invited the Association to meet next year at Appleton, Wisconsin.

Members of the organizing committee include the following:

Name	*Institution*	*Representing*
J. B. Culbertson	Cornell College	Iowa
D. W. Gier	Park College	Missouri
Edward L. Haenisch	Wabash College	Indiana
Fred Mathews	Beloit College	Wisconsin
Perry A. Moore	Hamline University	Minnesota
Ben T. Shawver	Monmouth College	Illinois
Gerrit Van Zyl	Hope College	Michigan

Edward L. Haenisch and Ben T. Shawver were elected as chairman and secretary, respectively.

The following seem to have been among the factors which gave rise to the formation of the Association: (1) a widely shared feeling of satisfaction in the discussion of common teaching and administrative problems, and (2) the prior nonexistence of a regional organization serving to bring so many people interested in college chemistry teaching together.

BEN T. SHAWVER

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● CHEMISTRY OF CARBON COMPOUNDS. VOLUME 1[A]. GENERAL INTRODUCTION AND ALIPHATIC COMPOUNDS

Edited by *E. H. Rodd.* Elsevier Publishing Co., Houston, Texas, 1951. xv + 777 pp. Illustrated. 16 × 23.5 cm. Subscription price, $18.00; single volume, $20.70.

THERE is great need for an up-to-date, authoritative reference work intermediate in size between Beilstein's "Handbuch der organischen Chemie" on the one hand and the more comprehensive textbooks such as "Karrer" on the other. One of the chief objects of such a reference work is to provide a handy source of information about important subjects and compounds along with a selected digest of references which will enable the practicing organic chemist to go quickly to the pertinent original literature or, where they exist, to more extensive secondary sources where complete references and a critical consideration are given. Another object is to summarize the literature not yet included in "Beilstein" on such compounds. The first object was attained to a remarkable degree by Meyer and Jacobsen's "Lehrbuch der organischen Chemie" and to a lesser extent by the various editions of Richter's "Organic Chemistry." It is probably impossible today to duplicate at a price within the reach of individual organic chemists the coverage attained by the former. The editors are seeking to make the present series a successor to "Richter" and in the first volume the literature of the classes of compounds included is covered to approximately the same extent. The general plan of the two series also appears to be similar.

In the present work there has been marked expansion of the space devoted to introductory chapters (from 89 pages in the third English edition to 217 pages). These chapters have been written by outstanding authorities and are very worth while reading, although they do not contribute greatly to the reference value of the series. The chapter on quantitative analysis of carbon compounds by R. Belcher is especially valuable because it gives the most recent methods and discusses them critically. Many will disagree with the conclusion that in general semimicro methods have the advantage over macro methods, but it is interesting to have the comparison detailed. The other ten chapters in this section include an historical introduction on the structure of organic compounds, a short outline of classification and nomenclature, and a far-too-brief section on literature and documentation, all by the editor. H. D. Springall has contributed a discussion of physical properties and a brief section on modern concepts of acids and bases. The latter will be unpopular in this country because it dismisses the widely used Lewis Concept in a short, uncomplimentary paragraph. A short chapter on crystallography by A. F. Wells is noteworthy for the clarity with which it presents the limitations of X-ray methods as applied to organic compounds. Chapters on light absorption by E. A. Braude, stereochemistry by E. E. Turner, mechanisms by E. D. Hughes, and free radicals by D. H. Hey and W. A. Waters conclude this first portion of the book. The discussion of mechanisms is a brief summary emphasizing especially the work of Ingold, Hughes, and their collaborators. It is gratifying that no signs are placed on the symbols for the various electronic effects (*I*, *E*, *T*, etc.), which is probably the best way to overcome the confusion caused by conflicting conventions. Unfortunately, Professor Springall in his chapters has chosen to retain the Robinson convention for the inductive effect although it is probably less widely used.

The remainder of the volume (510 pages) is devoted to a systematic presentation of aliphatic chemistry through the mono-

functional compounds and the following bifunctional classes: glycols, hydroxycarbonyl compounds, and dicarbonyl compounds. The writers of these sections are mainly younger British chemists in university positions. A. W. Johnson, well known for his monographs on acetylenic compounds, heads a rather large group from Cambridge University which has contributed eight of the eleven chapters. All of the chapters are uniformly good. The literature is covered to the extent projected, references are mostly well chosen, and British papers are not given undue prominence. Some improvement could be effected if the limitations of synthetic methods were given more carefully. When dealing with individual compounds, it would be helpful to have more often an evaluation of synthetic methods or at least an indication of methods of only historical importance or of little synthetic value. In this respect it is interesting to compare the present work with the recent revision of Whitmore's "Organic Chemistry." In the latter more attention has been given to individual compounds and to practical aspects of their laboratory and industrial synthesis. There is also less introductory material of a purely elementary nature in "Whitmore," so that space is saved without detracting from the value of the book. It is convenient to have both volumes available for quick reference because they are frequently supplementary to one another. This reviewer is of the opinion that for the classes of compounds treated in Volume I^A of the new series, "Whitmore" is slightly better, but this is unlikely to hold for future classes where the much shorter "Whitmore" is less adequate.

The index of a reference work is of great importance for its usefulness. Individual compounds appear to be carefully covered in the index of the volume under consideration, but subjects receive incomplete listing. Spot checking reveals that under the entry "allyl position" for instance, three entries are given, but the most important one (pages 208–9) has been omitted, as well as a shorter reference (page 280). Under "esterification" the principal reference (page 581 ff.) has been omitted. Other examples are easily found. It is to be hoped that in the general index, scheduled for Volume V, an effort will be made to correct these omissions and to distinguish clearly between the principal and the subsidiary references to each subject and compound.

In conclusion, it may be said that this first volume of "Chemistry of Carbon Compounds" gives promise that the series will achieve moderately well the objectives mentioned earlier. This reference work belongs on the shelves of scientific libraries in all universities, colleges, and industrial organizations. It will also be most useful to the practicing organic chemist if he can afford the high price (nearer $100 than $90 even on subscription if Volume I^A is a criterion), but the extravagant claim that "it will provide the most authoritative information and guidance on practically every fact he needs in his daily work" must be discounted.

THOMAS L. JACOBS

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● THE SECRET OF LIGHT

Irving Adler. **International Publishing Co., Inc., New York, 1952. 96 pp. Illustrated. 14 × 21.5. $2.25.**

Irving Adler writes a young world book about light that is easy to read and beautifully illustrated by Ida Weisburd's many illustrations that are important but fun to look at. Step by step, from ordinary mirrors and lenses to the atom, the reader is taken on an exciting trip through this unusual science book for teen-agers (and their parents and teachers, too). Before we know it, we have received a sound introduction to physics and chemistry as well as a discussion of how scientific theory has arisen out of man's practical work. Such a book is a welcome addition to any library.

GRETA OPPE

Ball High School
Galveston, Texas

THE UNIVERSITY LIBRARIES OF GEORGIA

● SMITH'S INTRODUCTORY COLLEGE CHEMISTRY

***William F. Ehret,* Professor of Chemistry, New York University. Third edition. Appleton-Century-Crofts, Inc., New York, 1950. x + 511 pp. 198 figs. 18.5 × 25.5 cm. $4.50.**

That the past has had an even greater than usual influence on this text is recognized in its title. "The present volume is a thorough revision of *Smith's Introductory College Chemistry* by James Kendall (1938). . . . The present revision adheres as closely as possible to the principle of 'progressive repetition' established as a working formula by Alexander Smith in his first text in 1906:

"No conception is defined and no generalization or law is developed, until such a point has been reached that applications of the conception and experimental illustrations, later to be related in the law, have *already* been encountered, and there is about to be occasion for further applications and illustrations of the same things in the chapters immediately succeeding. In these chapters the applications are frequent and explicit. Later page references and parentheses continue to indicate the recurrence of examples which might otherwise fail to be noticed."

While this approach has been assiduously retained, the present volume differs considerably from its preceding edition. Instead of the small pages of the predecessor, the third edition is printed on comparatively large, double-column pages, and its total number of words has been almost doubled.

There is considerable cross indexing, forward as well as back.

References for student reading, mostly to articles in the Journal of Chemical Education, have been added at the ends of most chapters.

Nomenclature of compounds has been changed. Recommendations of the International Union of Chemistry (*J. Am. Chem. Soc.*, **63**, 889 (1941); *Chem. Abs.*, **39**, 5869 (1945)) are followed. Fe_2O_3 is named iron (III) oxide; $Cu(NH_3)_2Cl$ is diammine copper (I) chloride. Older names are sometimes added in parentheses.

The earlier editions used molecular equations almost exclusively. This edition, however, uses many ionic equations, written in the form illustrated by the following from page 225:

$$2NH_4^+, CO_3^{2-} + 2(Cu^{2+}, 2NO_3^-) + H_2O \rightarrow Cu(OH)_2, CuCO_3\downarrow + 2(NH_4^+, NO_3^-) + 2(H^+, NO_3^-)$$

(This particular example is quoted because it illustrates a number of the conventions followed. It, like quite a few of the others, requires more than one line because of the narrow columns.) Substances that do not participate in the reaction are frequently retained in the equations. For some reasons, when heat is included in an equation it is always written on the *right* side, with the appropriate plus or minus sign, and similarly whenever electrons appear in equations (half-reactions) the electrons are invariably written on the *left* side.

In general, the book emphasizes a historical approach, sometimes unduly, and in some places it never gets around to modern ideas. Thus, atomic weights are defined only as relative. Page 152 states: ". . .sea-water contains bromine (in the form of sodium bromide). . . ." Page 156 speaks of the oil-well brines of southern California "which contain from 30 to 70 parts per million of iodine in the form of sodium iodide." The term "vapor tension" is retained, and is distinguished from "vapor pressure" (page 86).

Many will disagree with the author's hierarchy of hypothesis, theory, and law. ("If the *theory* stands the test of time,. . .it is finally called a *law*." (page 3)) (*Cf.* page 170.)

For the most part the descriptive chapters are quite traditional except for the greater emphasis on repetition and cross indexing. Iron is discussed in the very last chapter (Chapter 49), and some instructors may consider this rather late for so important an element.

Mass-action calculations and equilibrium constants are explained in Chapter 21, then used in later chapters. Both the Arrhenius and Brönsted definitions of acids and bases are presented; the former is used unless the latter is definitely needed.

Many would prefer earlier and greater emphasis on atomic structure. Nowhere in the book is there a complete listing of electron configurations by principal quantum groups (2, 8, 18, 8; etc.). (Such a table would be particularly helpful in Chapter 20: Electronic Structure and Chemical Properties.) In general, at the beginning of descriptive chapters, electron configurations are listed for the elements to be discussed. A complete listing by subgroups (2; 2,6; 2,6,10; 2,6) is given in Appendix VI. A long form of the periodic table is used, and includes atomic numbers (which were not included in the periodic table of the preceding edition!). Influence of Atomic Size upon Physical Properties is discussed on page 385 (more than three-fourths of the way through the book), followed by the statement: "That the relative sizes of atoms should be important in determining *chemical properties* has already been hinted at (page 211) and will be developed more fully now, (page 385)." The concept of kernel charge is never developed nor effectively used.

Often the author tends to emphasize rules instead of reasons. (*Cf.* properties of ionic *vs.* covalent compounds, page 207, for example.) Errors of fact occur occasionally. (In the fission of U^{235}, "neutrons are shot off with an energy of 200 million electron volts each." (page 182).)

However, in general the book is very carefully and well written. It is attractively printed, contains excellent diagrams, many excellent problems, and has very few typographical errors.

WILLIAM E. MORRELL

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● COLLEGE CHEMISTRY

***Paul R. Frey,* Professor of Chemistry, Colorado Agricultural and Mechanical College. Prentice-Hall, Inc., New York 1952. xxxvi + 653 pp. Illustrated. 23 × 15 cm. $5.95.**

CONSIDERABLE attention is being paid of late to the course in general chemistry. Although this course often is designed to meet the requirements of students in other fields as well as those preparing for a career in science, there is now a strong tendency to separate chemistry students into at least two beginning courses. The book under review is designed for those whose interest in science is already well-established.

An examination of the mechanical features of the book makes this purpose clear. The 36 chapters are well set up and are packed with useful information and carefully explained principles. Scattered through the text are many, many chemical equations. At the end of each chapter is a reasonable set of exercises. Those that call for a written answer are not always as carefully expressed as those calling for a numerical answer.

In the early chapters numerical exercises outnumber the others two to one, but this situation is reversed in the later, more descriptive chapters. The numerical exercises are separated into two categories according to difficulty. The index is good, but not as complete as it should be if students are to keep this book as a reference. For example, the word "binary" is used on page 65, but is defined later. Until the reader thinks of looking in the index under "Compounds, naming of," the definition on page 92 remains coyly hidden. At the end of each chapter there is a carefully chosen list of two or three films, and there are a number of references to articles in periodicals. The major source of these articles is the JOURNAL OF CHEMICAL EDUCATION. Book references are included in an appendix of 115 items. Most of these references are of the "magic-in-a-bottle" variety, but one looks for and finds, Mary Elvira Weeks, Bragg, Jeans, and Eddington. An unusual feature is the inclusion at the end of each chapter of a list of lecture-demonstration experiments. Although these directions are most convenient, the purpose is occasionally in doubt. This doubt is most evident on pages 66–7 where it is hard to decide whether the directions are for the benefit of the students or of the teacher. The discussion of the mechanical features of the book will be concluded with a word or two about the illustrations. The photographs are well-chosen and respectably few in number. The mat seems rather coarse but such evidence of disdain may possibly be premeditated. The line diagrams are charming but indecisive.

Although the form of the book clearly indicates that it is intended for science majors, the reasons given for paying attention to particular topics in the particular way are not clearly established. For example, the second sentence in the preface states that future developments in chemistry will be based upon the unchanging principles treated in the book. On page 19 we are told that our fundamental concepts concerning the nature of matter are changing rapidly, and a few lines later that the study of chemistry is a study of the physical and chemical properties of the elements. Again, the explicit purpose for the study of the periodicity of the elements is said to be that such study makes the remembrance of facts easier, but having said it, the author proceeds to utilize the principles of Mendeleev, Moseley, and a host of other men in such a way as to reveal much of the power and beauty of the intellectual structure formed by these principles. Explicitly, the philosophy of the text is confused although implicitly it is sound.

Perhaps part of this soundness derives from the fact that the writing is admirably restrained throughout. There is no striving for effect. The language is appropriate. Usually, the sentences are short, a first-class aid to clarity. This restraint is most effective in the final chapter of the book telling the story of nuclear energy.

Not all is made clear. Although the explanation of "mass" on page two leaves nothing to be desired, the explanation of "mass spectrograph" on page 46 is confusing.

The methods of solving problems shown in the worked examples stresses the algebraic treatment of dimensions as well as of quantities, an emphasis that is wholly admirable.

In spite of certain imperfections, this new text will probably be successful. Most of the topics ordinarily included in a beginning course are to be found in it and these topics are arranged in an orderly fashion. The treatment is rigorous, but fairly easy to follow. There is an abundance of suitable exercises, and judicious use of the demonstrations described will make it easy for the teacher to maintain student interest.

BENTLEY EDWARDS

CHICO STATE COLLEGE
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● THE CHEMISTRY OF ORGANIC COMPOUNDS

***James Bryant Conant,* President of Harvard University, and *Albert Harold Blatt,* Professor of Chemistry, Queens College. Fourth edition. The Macmillan Company, New York, 1952. viii + 655 pp. 21 figs. Tables. 16.5 × 24 cm. $5.90.**

THE fourth edition of this prominent textbook is a revision which differs from its predecessor mainly because of the addition of "certain new material dealing with the mechanisms of organic reactions and the directions which the reactions take." Perhaps the direction taken in this revision was prompted as much by current fashion as by good pedagogy. The authors have used discretion and restraint with respect to placement and volume of this new material. As to placement, "the discussion of each reaction mechanism is introduced in connection with a reaction to which it applies, rather than in a separate section on mechanisms." Because this text is an elementary treatment of the chemistry of organic compounds, it seems in order for the authors to expect that an elaborate treatment of electronic structures and reaction mechanisms be reserved for an advanced course. The selection of new material is such that the balance between classic organic and the "mechanics" of organic chemistry seems fairly satisfactory. The size of the text has not been increased, and so some of the classic organic in the third edition has been deleted.

The format and typography are essentially the same as in the third edition, except that chapter titles and section headings are now marginal rather than page-centered. In all but three minor instances chapter headings are the same as before. The

only rearrangement in the order of presentation places the discussion of organic acids after the chapter on aldehydes and ketones instead of before the chapter on gasoline and rubber. This appears to be a decided improvement. The questions and problems at the end of each chapter have been revised. In many cases the exercises are the same, the only change being in the order of arrangement.

The discussion of heterocyclic compounds has been revised completely to produce a palatable treatment. The chapter on natural and synthetic drugs is essentially the same, except for the addition of brief sections on drug antagonism and plant hormones. The most obvious deletion from the third edition is the separate treatment of the polyhalogen compounds. In the chapter on certain biochemical processes, the section on metabolism of carbohydrates has been shortened.

Perhaps the most obvious improvements in presentation are found in the chapter on alkyl halides and ethers, in discussions of addition to unsaturated systems and the interpretation of orientation rules in aromatic substitution. The suffix, *-yne*, is used exclusively in the nomenclature of the acetylenic hydrocarbons. Except for this discussion of systematic nomenclature appears to be the same as in the third edition.

Perhaps some teachers may feel that this text continues to follow too closely the traditional and conservative approach. Other teachers will maintain that the authors are much more pedagogically honest than authors of certain current texts. All teachers should agree that this revision has a singularly distinctive quality quite in harmony with the ability, interest, and requirements of most students who take a year's course in organic chemistry.

DONALD C. GREGG

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• ADVANCES IN CARBOHYDRATE CHEMISTRY. VOLUME VI

Edited by *Claude S. Hudson*, National Institute of Health, and *Sidney M. Cantor*, American Sugar Refining Company. Associate Editors for the British Isles, *Stanley Peat*, University College of North Wales and *Maurice Stacey*, The University of Birmingham. Academic Press, Inc., New York, 1951. xi + 442 pp. Illustrated. 15.5 × 23.5 cm. $8.50.

THE high quality of the earlier volumes in this important series is sustained by the present volume. Ten more topics closely related to the chemistry of carbohydrates are critically reviewed and thus made available to students and experienced chemists who find difficulty in keeping up with development in this rapidly expanding field.

Fundamental chemistry is rather heavily emphasized in this volume with chapters devoted to: The Methyl Ethers of *d*-Galactose (D. J. Bell), The Synthesis of Oligosaccharides (W. L. Evans), The Formation of Furan Compounds from Hexoses (F. H. Newth), Cuprammonium-Glycoside Complexes (Richard E. Reeves), The Chemistry of Ribose (Roger W. Jeanloz and Hewitt G. Fletcher, Jr.), The 2-(Aldo-polyhydroxyalkyl) Benzimidozoles (Nelson K. Richtmeyer), Friedel-Crafts and Grignard Processes in the Carbohydrate Series (William A. Bonner), and the Nitromethane and 2-Nitroethanol Syntheses (John C. Sowden). Of more descriptive interest is the chapter, Acoritic Acid, a By-Product in the Manufacture of Sugar (Roger Ellsworth Miller and Sidney M. Cantor). The chapter on Trends in the Development of Granular Adsorbents for Sugar Refining (Elliott P. Barrett) describes practical measures which are being taken to find a satisfactory substitute for bone char, the time-honored absorbent used in the sugar industry.

Some of these chapters represent tabulations of compounds of interest only to carbohydrate specialists. Others describe interesting organic reactions which can be carried out using carbohydrates as starting materials. Still others, such as the chapter on Nitromethane and Nitroethane Synthesis, describe new and improved ways for carrying out some of the classical operations of carbohydrate chemistry such as increasing the carbon chain and the formation of ketoses with a greater number of carbon atoms.

Of especial interest in this volume is E. L. Hirst's short but appreciative discussion of the life and accomplishments of Sir Walter Norman Haworth. The sudden death in 1950 of this great man took away one of the most distinguished and influential workers in carbohydrate chemistry.

IRWIN B. DOUGLASS

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• ADVANCES IN PROTEIN CHEMISTRY. VOLUME VII

Edited by *M. L. Anson*, Lever Brothers Co., *Kenneth Bailey*, University of Cambridge, and *John T. Edsall*, Harvard Medical School. Academic Press, Inc., 1952. vii + 411 pp. Illustrated. 16 × 23.5 cm. $8.50.

THIS seventh volume of an interesting and valuable series of annual essays on selected topics in protein chemistry maintains the same high standards set in earlier volumes.

The first review in the present volume is by F. Sanger on "The Arrangement of Amino Acids in Proteins." This significant approach, one of the most spectacular in modern protein chemistry, has been concerned with the complex problem of determining the position of individual amino acid residues in proteins. The review itself, as its author frankly states, ". . .has centered largely on the development of methods. . .and their uses (rather) than a discussion of results, which are still rather few." The use of 1 : 2 : 4-fluorodinitrobenzene, and other N-substituents for so-called "end-group" analysis are carefully described, and the methods for the degradation of proteins critically discussed. Briefly, the basis of the method is the reaction of intact protein with an agent which combines specifically with certain free groups, and then to carefully degrade the protein in such a way that the amino acid or peptide combined with this agent can be determined, and its position in the peptide chain ascertained. Application of the procedure to certain proteins such as egg albumin reveals no terminal residue with a free α-amino group, thereby suggesting that these proteins exist as cyclic peptides. Much work remains to be done before the full possibilities of the procedures discussed by Dr. Sanger may be considered to be adequately explored. This brilliant exposition tells us what so far has been accomplished, and what may be hoped for.

The next three reviews in the volume form something of a block. They are "The Structure of Collagen Fibrils," by Richard S. Bear, "Muscle Contraction and Fibrous Muscle Proteins," by Hans H. Weber and H. Portzehl, and "The Proteins of the Mammalian Epidermis," by K. M. Rudall. The block referred to is based upon the fact that all three reviews are concerned with groups of proteins in particular morphologic structure, rather than with individually characterized proteins, and that these groups are characterized to a greater extent physically than chemically. The review by Dr. Bear is almost entirely based on X-ray spectra of the collagen fibrils, and this biophysical criterion is also employed in the other two reviews to characterize the muscle and epidermic proteins, respectively. It is of interest to note that nearly all of Dr. Rudall's review is based upon his own work with cow's nose epidermis, apparently a good material for the purpose intended; one misses in this review some consideration of the extensive work on human and mouse epidermis by Cowdry and his associates at the Barnard Free Skin and Cancer Hospital in St. Louis.

The last two reviews in the volume also fall together, for they cover "Infrared Analysis of the Structure of Amino Acids, Polypeptides, and Proteins," by G. B. B. M. Sutherland, and "Ultraviolet Absorption Spectra of Proteins and Amino Acids," by G. H. Beaven and E. R. Holiday. Both reviews are quite valuable and cover a wide range of spectral phenomena. One

would have liked to see some mention of the ultraviolet spectra of dehydropeptides in the latter review. One inadvertent slip in this review was noted on page 378 where the authors state that no reports of the synthesis of tripeptides with an aromatic acid in the middle have come to their notice. Emil Fischer synthesized such a compound, namely, glycyltyrosylglycine, (*Ber. Chem. Ges.*, **41**, 2860 (1908)).

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● THE ORIGIN OF LIFE AND THE EVOLUTION OF LIVING THINGS

Olan R. Hyndman. **Philosophical Library, New York, 1952. xxi + 648 pp. 42 figs. 2 charts. 15.5 × 23.5 cm. $8.75.**

Evolution takes place, according to this theory, somewhat in this manner: The basic unit is the germ integer, which by a process of "retracement" or resynthesis of itself, follows the chronological order of evolution. The germ integer imposes a "chromatin stencil" which is composed of "phylogenetically accrued increments upon development"; the "chromatin stencil" is a result of response to environmental forces, acting first on cytoplasm and then to the germ cell to establish "parallel genetic organization" which is carried forth. In other words, the author is proposing a theory based on the inheritance of acquired characters, in which the organism reacts to the environment rather than being selected by it. There seems to be little original observation in this book and not much effort to verify facts. For example, in commenting on the report that there are two polar bodies given off during maturation in the male honey bee, he writes, "In keeping with the formula which I have been following, I would not expect this to be the case." Many of the statements are superficially similar to recent work in genetics, but the requisite critical attitude is not there.

The ideas could have been more lucidly presented, and certainly should have been more concisely put. There are somewhere between 250,000 and 280,000 words in this book, although only 38 references are listed, and many citations appear to be second-hand from these works, which include a large number of elementary texts. The omission of most of the recent monographs on evolution is conspicuous. If the author desires a critical reading, he should publish a short version with better documentation.

JOEL W. HEDGPETH

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● CARBON DIOXIDE FIXATION AND PHOTOSYNTHESIS

Number V of The Symposia of the Society for Experimental Biology. Published for the Company of Biologists on behalf of the Society for Experimental Biology. Academic Press Inc., New York, 1951. vi + 342 pp. Illustrated. 16 × 25.5 cm. $6.80.

The (British) Society for Experimental Biology brings together every year, a select group of researchers to discuss an important topic in biology or biochemistry. With the giant meetings of the main professional societies becoming more and more crowded with thousands of people, hundreds of five-minute lectures, and dozens of social events and exhibitions, and thus less and less productive of fruitful exchange of scientific ideas, such smaller gatherings grow increasingly indispensable for the advancement of science. The long established symposia of the Faraday Society on various topics of physical chemistry, and the Symposia of the Society of Experimental Biology, give England a leadership in this field; the Cold Spring Harbor Symposia on Quantitative Biology are an example of the equally distinguished annual gathering in America. In addition to such regular affairs, more and more *ad hoc* conferences are being arranged, here and abroad, to bring together men and women working in a specific field, and it is only to be hoped that the brutal interference with the travel of foreign scientists to America, which has followed the adoption of the McCarran Act, will not for long cripple the organization of such research conferences in America.

The fifth volume of the "Symposia of the Society for Experimental Biology" contains twenty-one papers on Carbon Dioxide Fixation and Photosynthesis, presented in July, 1950, at Sheffield, England. The ground covered is partly the same as in the volume "Photosynthesis in Plants" of the American Society of Plant Physiologists (Ames, Iowa, 1949), but the present collection also includes five papers on non-photochemical carbon dioxide metabolism in animal and plant tissues, and three papers on fundamental aspects of photochemical processes in solutions. Practically every paper is by a foremost specialist in the field. The volume is therefore of the greatest interest for everyone who works on photosynthesis or on carbon dioxide metabolism in general. It is not suitable—and is not intended—to serve as an introduction into the field for the general reader; but individual papers in it could be very useful for reviewing by advanced biology students in seminars and journal clubs.

The format and typography of the volume are particularly pleasant.

EUGENE RABINOVITCH

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● THE RISE OF THE NEW PHYSICS

A. D'Abro. **Second edition. Dover Publications, Inc., New York, 1951. ix + 426 pp. 37 figs. 36 portraits. 14.5 × 21 cm. $8 for set, Vol. I and II.**

This work is a reprint of the author's "The Decline of Mechanism" published by D. Van Nostrand Co. in 1939. With the appearance of the new edition certain corrections have been made and 36 portraits of mathematicians and physicists have been added to enhance the historical flavor.

Mr. D'Abro's book is an ambitious undertaking, since it endeavors to review in semi-popular fashion the fundamentals of physical methodology, the concepts of classical physics, and the methods of modern quantum mechanics. Each of these topics is worthy of a book in its own right and it is not surprising that the author has found it necessary to extend his treatment to nearly 1000 pages. As was the case in his earlier work, "The Evolution of Scientific Thought from Newton to Einstein," the author's style is generally clear and attractive and in much of the book he succeeds rather well in bringing out the essential meaning of modern physics in readable and reliable fashion with a minimum of mathematics. The latter part of the program breaks down indeed when quantum mechanics is reached (the final 400 pages) and the reader must be contented here with the conventional analytical treatment enlivened indeed with generous heuristic considerations and verbal amplifications of knotty points. The professional student of quantum mechanics could do worse than use this part of the book as a supplement to the standard treatises.

The elementary presentation of the types of mathematics used in the development of physical theories (100 pages more or less) will doubtless appeal to many readers who have neither the ability nor the time to wade through treatises in mathematical physics. They will at any rate get a glimpse of what goes on in the application of mathematics to physics.

In an elaborate work of this kind it is inevitable that questionable statements and points of view will occasionally occur. The reviewer might note in the historical sections, for example, the attribution of the law of refraction of light to Descartes, and the failure to do complete justice to the really fundamental character of the postulates of the Bohr theory of atomic structure. In his methodological discussion the author (page 93)

seems to give a misleading impression of both the physical power and the possible mathematical elaborateness of thermodynamics. Nothing is said about the postulational development of Carathéodory nor is there any reference to the important new work on the thermodynamics of irreversible systems. The discussion of wave propagation (pages 269 ff), to cite another example, is misleading since it is unnecessarily restricted to *periodic* waves.

The recent papers of Schrödinger suggest that the problem of the interpretation of quantum mechanics, usually considered to have been settled by the probability view of Born, may have to be reopened for more careful consideration.

The portraits of famous mathematicians and physicists add considerable interest to the work. Among those of pre-quantum physicists is one said to be that of Lazare Carnot (1753–1823). This gentleman was not a physicist but a military expert whose principal scientific contributions were in the field of mathematics. His elder son, Sadi Carnot (1796–1832), was the eminent physicist, known to fame as one of the founders of thermodynamics.

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• BIOCHEMICAL PREPARATIONS. VOLUME 2

***Eric G. Ball*, Editor-in-chief. John Wiley & Sons, Inc., New York, 1952. vii + 109 pp. 2 figs. 15.5 × 23.5 cm. $3.**

In recent years the study of individual chemical reactions in animal and plant tissues has occupied a large segment of biochemical research. Such studies necessitate the isolation or preparation of components of enzyme systems. For this reason a compilation of reliable methods for obtaining highly purified substances of biochemical interest is quite desirable. Such a compilation is the objective of "Biochemical Preparations."

The present volume is the second in the series. It contains isolation procedures for cytochrome-*c*, seed globulin, phosvitin, lactic dehydrogenase, oleic acid and methyl ricinoleate; the biosynthesis of myo- and epi-inosose, inositol monophosphate and C_{14}-labled sucrose. In addition, chemical procedures for the preparation of 14 compounds of biochemical interest are described.

The methods are presented with full details of procedure and are supplemented with footnotes in which choice of reagents, yields, and other helpful comments appear. Each method has been checked by independent workers which insures that those who follow the directions will probably find them adequate.

Undoubtedly, future volumes in this series will include methods for the isolation of more of the enzyme proteins when methods for their preparation are perfected. As this series of volumes expands, it will be of value if each volume contains a list of the compounds that have been described in the earlier volumes of the series.

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• METALLURGICAL ENGINEERING. VOLUME I. ENGINEERING PRINCIPLES

***Reinhardt Schuhmann, Jr.*, Associate Professor of Metallurgy, Massachusetts Institute of Technology. Addison-Wesley Press, Inc., Cambridge, Mass., 1952. ix + 390 pp. 155 figs. 19 × 25 cm. $7.50.**

"The past ten years have brought general recognition of the fact that the traditional college training in the established arts of extracting the common metals from their ores no longer is the soundest basis for a successful career in the metallurgical profession. One major factor in the awakening has been the rapidly expanding contributions of chemical thermodynamics to the solution of practical metallurgical problems. It is a little disturbing to find that many of these contributions have been made by chemists with little or no formal metallurgial education. Another significant trend has been the increasingly prominent role of chemical engineers in metallurgical activities."

Thus a metallurgist admits the superiority of training in fundamentals over descriptive technology. He proposes to apply some of these fundamentals to process metallurgy. The successful application of the concept of unit physical operations and unit chemical processes in chemical engineering points the way to its application to metallurgy.

In the first volume the author devotes ten chapters to engineering principles common to all the unit processes of extractive metallurgy. These are: (1) The Unit Processes of Chemical Metallurgy, 11 pages; (2) Stoichiometry, 31 pages; (3) The Heat Balance, 26 pages; (4) Metallurgical Fuels, 40 pages; (5) Combustion of Fuels and Heat Utilization, 34 pages; (6) Fluid Flow, 48 pages; (7) Steady Heat Flow, 68 pages; (8) Unsteady Heat Flow, 25 pages; (9) Phases in Pyrometallurgical Systems, 41 pages; (10) Refractory Materials, 43 pages. In considering the number of topics, and the space allotted to each, that are covered in one semester, the reviewer wonders if the success of the chemist and chemical engineer is not due to the emphasis and time spent on fundamentals. The chemical engineer will spend a semester on stoichiometry alone.

The author has done an excellent job of reducing the fundamentals in each subject to a chapter of material that is applicable to process metallurgy. The chapters on fluid flow and heat transfer appeared particularly good. All chapters are concluded with problems that apply the principles to metallurgical problems.

Chemists and chemical engineers will be interested in seeing this "new look" given the teaching of metallurgy, particularly if they desire to adapt these industrial problems to their courses to extend the breadth of training of their students.

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• ANNUAL REVIEW OF NUCLEAR SCIENCE. VOLUME I

Committee on Nuclear Science, National Research Council. Annual Reviews, Inc., Stanford, Calif., 1952. ix + 645 pp. Illustrated. 15.5 × 23 cm. $6.

This first volume of the series planned to present the most significant developments in the various associated fields of nuclear science does somewhat more than its title implies. Most of its contributors not only review the published work in the year 1950, but attempt to provide sufficient background material to provide a true perspective for the year's advances. In many cases this is accomplished in a space-saving fashion by reference to a critically chosen bibliography of general reviews. This is a feature of the volume which particularly adds to its value for the academic library. Since the diversity of research in nuclear phenomena is so great, the comprehensive plan for the series seldom will allow a mere one-year appraisal of a topic to be made. This has been anticipated by many of the specialist contributors with an unusually large number of "in-press" and "private communication" references.

The spectrum of topics covered ranges from meson physics to plant nutrition. Of the 611 text pages, about half are devoted to topics primarily of interest to physicists, the other half to chemists and biochemists. Chemistry professors seeking an efficient means of keeping posted on the progress of other than their own specialities have been enthusiastically grateful for other Annual Review series. This first volume of a new series will most certainly receive the same response. Among the chapters included in this volume which are sure to be of interest to academic chemists are: Katz and Manning on "The chemistry of the actinides," Edwards on "Isotopic tracers in chemical systems"

Rodden's "Analytical nuclear chemistry," Clewett's encyclopedic "Chemical separation of stable isotopes," Rogers' and Spedding's discussions of the progress in the metallurgy of elements involved in nuclear reactor development, and the pair of chapters on biochemical research: Villee on radioisotopes and Rittenberg and Price on the use of stable isotopes.

Each chapter is accompanied by a bibliography including 1950 publications. The utility of these extensive literature compilations is further amplified by adequate indexes of both subjects and authors for the volume as a whole. The fact that all information in the book has received official security clearance gives it a definitive function which may be welcomed by those readers who have had intermittent access to the classified literature. The text gives evidence of careful editing; the figures are clearly drawn and well proportioned; the tables are well composed and gratifyingly uncrowded.

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● IMPERFECTIONS IN NEARLY PERFECT CRYSTALS

Edited by *W. Shockley, J. H. Hollomon, R. Maurer,* and *F. Seitz.* John Wiley & Sons, Inc., New York, 1952. xii + 490 pp. 173 figs. 14.5 × 22 cm. $7.50.

In this book are collected the papers presented at a conference on "Lattice Imperfections," held in October, 1950, under the sponsorship of the National Research Council Committee on Solids. The contributers are the following, all experts in this difficult but highly important field: L. Apker, B. L. Averbach, J. Bardeen, C. S. Barrett, R. G. Breckenridge, B. Chalmers, C. G. Dunn, J. C. Fisher, A. Guinier, C. Herring, J. S. Koehler, N. F. Mott, W. T. Read, Jr., F. Seitz, W. Shockley, C. S. Smith, R. Smoluchowski, E. Taft, B. E. Warren, and C. Zener.

In an excellent first chapter, Seitz deals with the various types of crystal imperfection and their interrelationships, showing how they may be considered from a unified viewpoint. The remaining chapters deal with special problems or methods of study. The emphasis in nearly all is on metals—methods of study, their imperfections and relations between these imperfections and physical properties. This is indeed an important subject and anyone specializing in the theory of metals will find this book invaluable. It is, however, surprising that, in a book having this title, there is no discussion of photographic behavior or phosphor activity, both of which depend so greatly on crystal imperfections. It is to be hoped that future conferences and books will deal in a correspondingly adequate manner with these fields.

In conclusion, it should be emphasized that this book is one for the specialist, not for classroom use or (except possibly for Seitz' first chapter) for casual reading by those in other fields.

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● PHOSPHORIC ACID, PHOSPHATES AND PHOSPHATIC FERTILIZERS

***William H. Waggaman,* Senior Mineral Technologist, Bureau of Mines, U. S. Deartment of the Interior. Second edition. Reinhold Publishing Corp., New York, 1952. vii + 683 pp. Illustrated 15.5 × 23.5 cm. $15.**

The second edition of this very useful technological reference work dealing with phosphorous and its many economically important derivatives is a most welcome addition to the literature of chemistry. When the first edition appeared in 1927 the superphosphate fertilizers represented the only important tonnage outlets for our tremendous phosphate resources. Although phosphatic fertilizers still are in top position, there are now many other important phosphorus products which have been made available as the result of tremendous advances in fundamental knowledge and technology of phosphorus and its compounds during the past quarter century.

In undertaking to prepare a completely new book on this subject, the author wisely chose to solicit the cooperation of specialists to write authoritative reviews on the various phases of phosphorus chemistry and technology. New developments in the production of phosphorus, and of phosphoric acid both by wet methods and directly from the element, are treated adequately. The production of such important tonnage items as the phosphatic fertilizers, the triple and concentrated superphosphates, the ammoniated products, and complete plant foods, is nowhere else covered in quite a satisfactory a manner as has been achieved by the author. Outstanding are the last few chapters dealing with the manufacture and applications of phosphates in baking powders, as water softening and cleaning agents, and as fire retardants. Recent commercial developments covering the use of alkyl and aryl phosphates as plasticizers and solvents are reviewed. The uses of phosphoric acid in the metal industry for building up corrosion-resistant films are presented in a manner which should appeal to metallurgists and chemists alike. Especially noteworthy are the discussions of the economic aspects of the raw material sources, products, and processes—phases of the subject in which the author has long been an accepted authority. In fact, it is only the introductory chapter which can be criticized for not being up to date. It is to be regretted that the author felt it necessary to use a foreign reference source carrying the date line 1928 for most of his information on phosphorus chemistry. Fortunately, none of the specialists who collaborated with him in writing more than half of the chapters of this edition is guilty of such errors in fact and theory as are found in Chapter I.

The appendix contains much information which will be useful to both the "technical man engaged in research and development" and "the plant superintendents and foremen." An extensive listing of U. S. patents pertaining to the manufacture and uses of phosphorus compounds is a distinctive feature. The subject matter index is good.

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● HYPERCONJUGATION

***John William Baker,* Reader in the Mechanism of Organic Reactions in the University of Leeds. Oxford University Press, London, 1952. vi + 158 pp. 4 figs. 13 tables. 14.5 × 22.5 cm. $3.50.**

This little monograph on hyperconjugation is a timely review of a subject which is exceedingly important in modern theoretical organic chemistry. It is written with keenly critical acumen in a style which is concise and clear—a statement which will occasion no surprise to those who have read Dr. Baker's previous monograph, "Tautomerism," and his many research papers. The modest size of the book was made possible by addressing it to those chemists who are thoroughly acquainted with the electronic theory of organic chemistry used by the English school.

The object of the monograph, as stated in its introduction, is to give a coherent review of hyperconjugation presenting the evidence "accumulated in support of the concept and to illustrate its increasing importance and significance in the theoretical interpretations of the reactions of organic chemistry." This goal was fully achieved. The physical evidence is introduced immediately after a historical introduction. The chemical evidence is, by its very nature, practically limited to showing that predictions made on the basis of the theory of hyperconjugation are in accord with experimental knowledge. This evidence is included in the remaining chapters which deal with aromatic substitution, tautomerism, addition reactions, elimination reactions, heterolytic alpha-methylenic reactions of olefins, and finally a chapter on homolytic reactions.

In an appendix Dr. Baker gives a complete summary of the nomenclature and symbols of the English school together with concise explanations of each such term and does it in only two and a quarter pages—an effective rebuttal to that small group of American chemists which apparently feels that the English nomenclature is so ridiculously complex that it merits no serious consideration.

It should be recalled that the theory of hyperconjugation was at one time known as the Baker-Nathan effect. Although it is not true that Baker and Nathan were the first to suggest the possibility of "no-bond resonance" (a term synonymous with hyperconjugation) it is true that the concept was almost never used in theoretical organic chemistry prior to their famous paper which appeared in the year 1935. Their success in using the concept was linked to the important assumption that only C–H linkages could become involved in hyperconjugative resonance. It is therefore particularly interesting to note that Dr. Baker now freely assumes the participation of carbon-halogen linkages in hyperconjugative resonance in both excited and ground states.

The presentation of the subject matter of the book is as rigidly limited to the theme of hyperconjugation as possible. However, in discussing the applications of the hyperconjugative concept to diverse organic reactions, Dr. Baker has found it expedient to introduce each new topic with at least one paragraph summarizing pertinent knowledge relating to the topic. This practice adds immeasurably to the value of the book, especially since Dr. Baker possesses to a remarkable degree the ability to summarize clearly and in a few words the information which is essential for the understanding of a topic. A good example is the introductory paragraph to Chapter IV in which he summarizes the modern theory of tautomeric equilibria. His discussion of organic reactions also includes many references to recent theoretical developments which have not for the most part been included at all in other books on theoretical organic chemistry.

It is the opinion of the present writer that all organic chemists seriously interested in the electronic theory of organic chemistry should read this monograph.

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• PRINCIPLES OF WEED CONTROL

Gilbert H. Ahlgren, **Professor of Farm Crops, Rutgers University and The State University of New Jersey;** ***Glenn C. Klingman,*** **Associate Professor of Agronomy, North Carolina State College; and** ***Dale E. Wolf,*** **Assistant Manager, Agricultural and Biological Section, Grasseli Chemicals Dept., E. I. du Pont de Nemours and Co. John Wiley & Sons, Inc., New York, 1951. vii + 368 pp. 109 figs. 25 tables. 14.5 × 22 cm. $5.50.**

WEEDS have been the bane of the farmer's existence since man first tilled the soil. It has been only in the past two decades that the character of weeds, their identification, dissemination, habits of growth, and eradication have been intensively studied. As a result of these studies more and more effective means of weed control are being developed.

The exact definition for a weed that would be universally applicable still defies the best efforts of man. A plant in one situation may be a weed but in yet another it may have considerable economic value. Similarly, since nature abhors a vacuum, many of these wild plants serve a useful purpose on waste lands by preventing soil errosion and at the same time building up the soil. This diversity of characteristics in plants when compounded with a wide variety of crops and situations under which the plant may occur gives a clue to the complexity of the problem of weed control.

Weed control involves the application of knowledge from such diverse fields as botany, agronomy, horticulture, chemistry, plant physiology, and ecology. The authors of this book have attempted to show a direct application of these various branches of science to the problem. The student will find a discussion of such diverse subjects as the chemistry of herbicides and their physiological effect, plant competition, and equipment for weed control in the book.

Each crop presents its own individual weed problem necessitating variation in the method of the application or chemical or other means of weed control. The cereal crops and grasslands come as close as any crops in similar requirement in control measures. 2,4-D has been especially outstanding for weed control in these crops, but other chemicals and other methods are required for certain specialized problems.

The increasing interest and importance of defoliation and preharvest maturation of certain crops to facilitate machine harvest provides another use for herbicides. The defoliation of cotton is extremely important to machine harvesting. For the first time this problem has been recognized to be of sufficient importance to have a chapter in a textbook devoted to it.

"Principles of Weed Control" is an interestingly written book. The student will also find the organization of material logical and easily understood. The organization of the book is a departure from similar texts, in that portions of it are devoted to weed problems by crops. On the other hand, research workers may be somewhat disappointed by the lack of depth of the information. Unfortunately, there is less emphasis devoted to the principle involved in the problem of controlling a given weed than there is in a description of currently employed practices. Moreover, the references cited at the end of each chapter are not as up to date as one might expect in a book published in September of 1951, nor are they particularly exhaustive. Frequently references are brought up only to 1949 and in many of these cases there are later references.

Illustrations in the book are generally good, but a few of the photographs show poor composition in that the presence of some individual or some item of equipment distracts from the point of the photograph.

As is frequently the case with early books in a new field, a few minor factual errors have crept in. This does not especially detract from the value of a well written book and can be overlooked in this case where the published information on points concerned is very very sketchy.

On the whole, the student and interested layman in this field will find interesting and informative reading in the book. While a research worker will certainly want this book on his shelf, he will not find it a particularly profound reference book.

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• ELEMENTARY HEAT POWER

H. L. Solberg, O. C. Cromer, **and** ***A. R. Spalding,*** **respectively Professor and Associate Professors of Mechanical Engineering at Purdue University. Second edition. John Wiley & Sons, Inc., New York, 1952. xvi + 624 pp. 308 figs. 13.5 × 22 cm. $6.50.**

THE second edition of this sucessful text in the heat power field has been expanded and kept up to date. It is essentially a text descriptive of equipment used in power generation. The first two chapters deal with fundamentals of thermodynamics and fuels and combustion. Thermodynamics can hardly be taught in the 63 pages devoted to it, particularly when units and dimensions, the gas laws, properties, the flow equation and the second law are all discussed. Nor can combustion calculations be covered in 49 pages that describe fuels, their properties and analysis, and the stoichiometry of combustion. At least, the authors define the pound-mole before tabulating formulas into which analytical values can be substituted.

The last eleven chapters are the best. They are descriptive of heat power equipment: internal-combustion engines, fuel-burning equipment, steam generation, steam power-plant cycles, steam turbines, steam engines, pumps, drafts, fans, blowers and

compressors, feed-water heaters and condensers, the gas-turbine power plant, and mechanical refrigeration. The descriptions are clear and well illustrated. The material is thoroughly modern, the aircraft gas-turbine is described (but not the ram-jet), and a description of the heat pump concludes the chapter on refrigeration.

This book is widely used in beginning courses in mechanical engineering heat power. If one desires a description of this type of equipment, this book is excellent.

KENNETH A. KOBE

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● THE PHYSICAL CHEMISTRY OF SURFACE FILMS

William D. Harkins, **University of Chicago. Foreword by *Peter Debye,* Cornell University. Reinhold Publishing Corp., New York, 1952. xvi + 413 pp. 214 figs. 15 × 23 cm. $10.**

THE name of Harkins has long been associated with fundamental studies of the nature and properties of surface films. It is indeed fortunate that, before he died last year, he was able to finish the writing of this book, in which he has summarized his ideas and the methods and results of his researches in this important field. Three of the chapters—those dealing with The Nature and Energetics of Surfaces, Films on Liquids, and Films on Solids—are revisions of articles published by him in the series of volumes on "Colloid Chemistry," edited by Jerome Alexander. To these Harkins has added new chapters on properties of soap solutions and mechanism of emulsion polymerization, the latter dealing with the author's important contributions to the synthetic rubber program during the recent war.

The final chapter is a reprint of an article on "The Role of the Electric Double Layer in the Behavior of Lyophobic Colloids" by the renowned Dutch physical chemist, E. J. W. Verwey. Harkins did not consider himself an expert in this field and so turned for help to someone who was.

Peter Debye has contributed an appreciative foreword and T. F. Young an excellent historical introduction, outlining Harkins' scientific career, with emphasis on its relationship to surface chemistry.

This book covers a very important subject. It is authoritative. The presentation is unusually clear and understandable. It should serve admirably as a textbook for an advanced course or as a source of background material for teachers of physical chemistry and for students considering entering this research field.

MAURICE L. HUGGINS

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● ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY VOLUME VIII: ION EXCHANGE TO METAL PLATING

Edited by *Raymond E. Kirk* and *Donald F. Othmer,* Professors and Heads, Departments of Chemistry and Chemical Engineering, respectively, at the Polytechnic Institute of Brooklyn. Assistant Editors, *Janet D. Scott* and *Anthony Standen.* The Interscience Encyclopedia, Inc., New York, 1952. xvi + 944 pp. 19 × 27 cm. Subscription price, $25. Single Volume, $30.

WITH the "Encyclopedia" now two-thirds completed the user of a technical library will have found that it is the first place to which he turns for both scientific and technological information. The more frequent cross references to previous volumes indicate the progressive completion of this extensive work.

Volume VIII leans heavily on the side of technology with extensive sections on ion exchange, lamp manufacture, laundering, leather and tanning, lignite, lime and limestone, linen, linoleum, lubrication and lubricants, luminescent materials, magnetic properties and separation, manufactured gas, margarine, matches, meat and meat products, metallic coatings and metallography.

The inorganic chemist will find the metals iron, lead, lithium, magnesium, and mercury, their alloys, compounds, and preparations. The section on isotopes is an excellent survey of this subject. The organic chemist will be particularly interested in the sections on isomerization, ketones, lactic acid, lactones, maleic acid, malonic acid, and mercaptans. The biochemist also has sections on lecithin, lignin, lipids, malaria chemotherapy, malts, and malting. The physical chemist will find only three sections of special interest: low temperature technique, mass spectroscopy, melting and freezing temperatures.

Two sections deserve special attention by all chemical personnel. The section on laboratories points out desirable construction features and safety precautions in the design of laboratories for general and special purposes. The lengthy section on the literature of chemical technology first surveys all the usual, and also uncommon, sources of chemical information and then shows how to set up this information on cards for subsequent mechanized searching.

In contradistinction to the letter *C* which occupied approximately two volumes, the letter *J* occupies only a half page of cross references.

The importance and value of the "Encyclopedia" to the small reference library becomes more and more apparent as completion of the set nears.

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THE UNIVERSITY OF TEXAS
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● TREATISE ON POWDER METALLURGY. VOLUME III: CLASSIFIED AND ANNOTATED BIBLIOGRAPHY

Claus G. Goetzel, **Vice-President and Director of Research, Sintercast Corporation of America, New York. Interscience Publishers, Inc., New York, 1952. xxiv + 899 pp. 16 × 23.5 cm. $22.**

REFERENCE is made to reviews of Volumes I and II of this treatise which appeared in earlier issues of THIS JOURNAL (**26**, 623; **28**, 613).

The third volume, as the subtitle implies, consists of Part One, a classified and annotated list covering the literature devoted to powder metallurgy; and Part Two, a classified and annotated list of patents. In addition, there is an eight-page patent cross index with references to Volumes I and II, a five-page subject index, and a 76-page name index. There are over 12,000 reference citations covering the literature up to January, 1950. A few items of later date are also included, particularly new editions of older books, or continuations of previously published works.

It will be of great convenience to research scientists and engineers alike to have at hand this guide to the extensive literature of powder metallurgy. The techniques of powder metallurgy are not only of use in producing machine parts, but are among the most valuable of research tools. The twelve-page table of contents and extensive indexes mentioned above make these techniques readily uncovered, even if they occur in obscure sources.

The author is to be congratulated on the scope of his project and the vigor and thoroughness with which he carried it out. One must also admire the audacity of the publishers in undertaking the publication of such a high-cost treatise for a rather limited audience. It is hoped that their confidence in this treatise is justified.

The three-volume set is recommended for the reference shelves of scientific libraries and for the desks of those who might profitably use the powder metallurgy approach for the solution of their problems.

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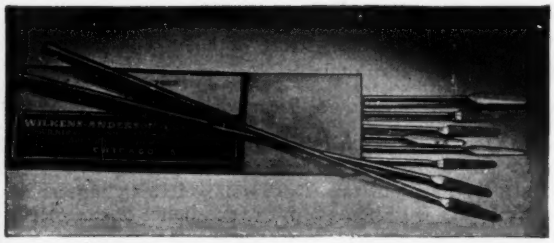

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References

(1) Ind. Eng. Chem. 25-653 (June, 1933)

(2) Ind. Eng. Chem. 25-1112 (Oct., 1933)

(3) National Bureau of Standards Journal of Research 12-241 (Feb. 1934, R.P. No. 649)

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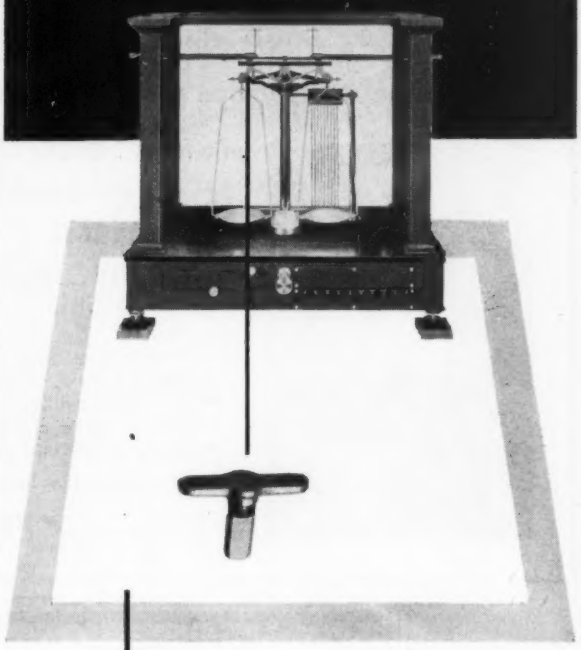

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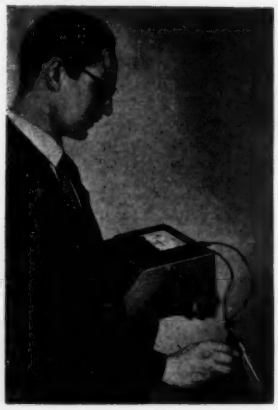

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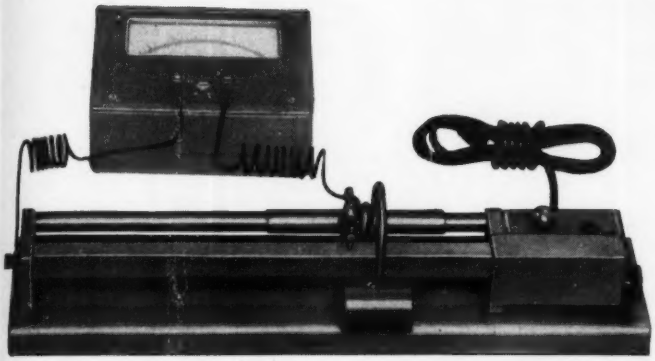

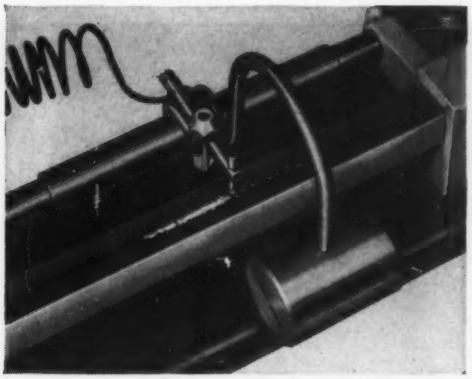

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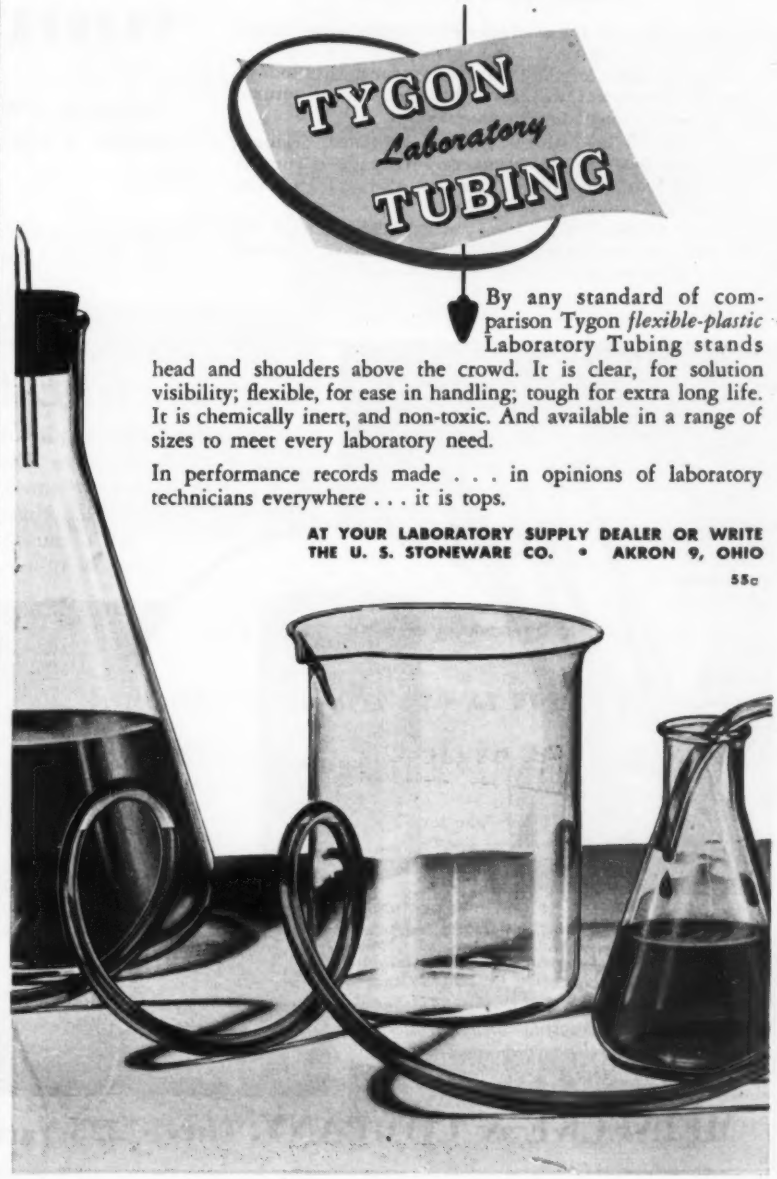

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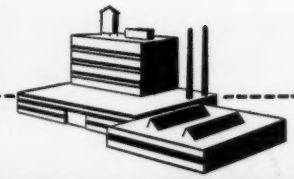

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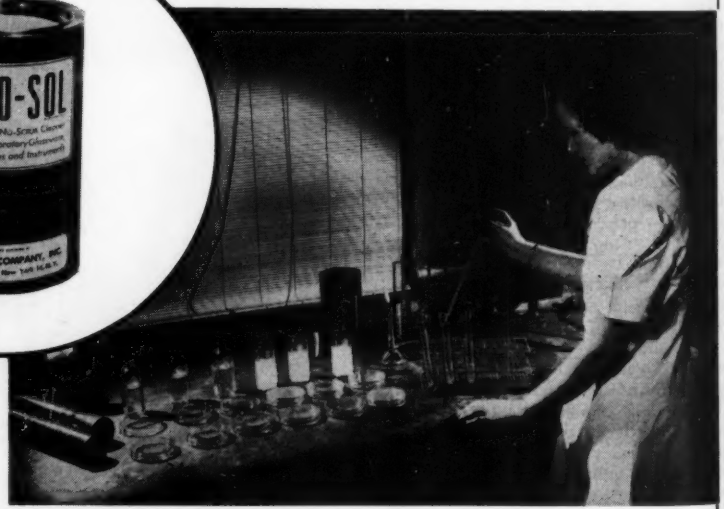

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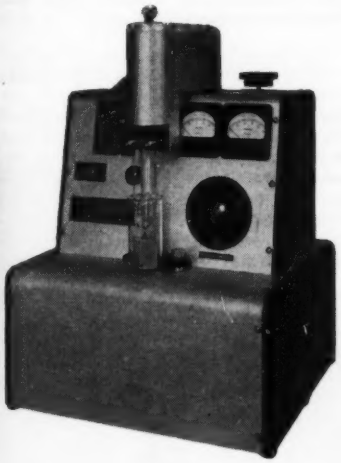

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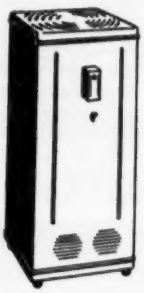

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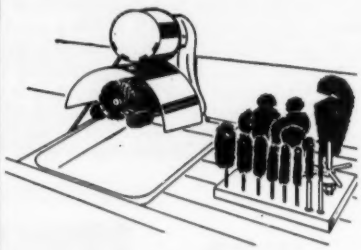
Fully automatic. Inexpensive to operate. Will service up to 13,500 cu. ft. Moisture removal rate: at least one pint of water per hour, at 80° F and 80% humidity. Humidistat permits operation only when humidity exceeds desired setting. Approximately 26" high, 13" square.

16942T For 115 volts, 60 cycles....$205.00



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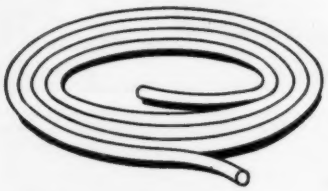

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23525T

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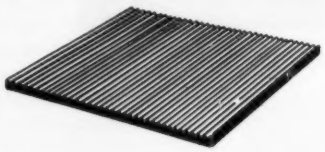

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and water supplied by means of a rubber tube connected to any cold water faucet.

Ease of operation is such that junior personnel or students can fractionate after a few hours of observation and instruction. When rate of flow, degree of vacuum, and temperature have been set on the easy-to-read panelboard controls, the new still requires almost no watching or adjustment.

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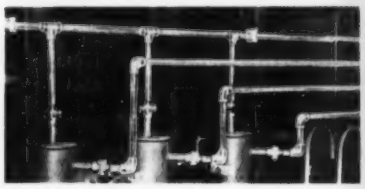
The new Asco High Vacuum Molecular Still is manufactured by the Asco Mfg. Co. of Webster, New York and is distributed exclusively in the U. S. by American Instrument Co., Inc., Silver Spring, Maryland.

New Transparent Plastic Pipe Has Many Laboratory Uses

Transparent plastic pipe fittings of cellulose acetate butyrate in sizes ranging from $\frac{1}{2}$ inch through 4 inches are now available for laboratory and pilot plant use. Known as Mills III, the new pipe offers many advantages for handling oils, gases, water, slurries, and a wide variety of chemicals because it permits observation of processes, and has extremely high resistance to corrosion and other forms of chemical attack.



Sections of the pipe are quickly and easily joined by a solvent cement that produces a leak-proof, homogeneous bond. No threading or special tools are required, even when connecting to standard steel pipe and fittings. Cuts easily with ordinary hand saw. Set-ups may be dismantled and all components used over and over again—alterations in any set-up can be made in minutes.

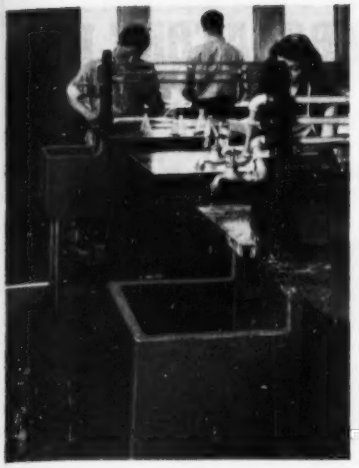
There are almost no limits to the laboratory uses of Mills III pipe. It is reasonable in cost, the smaller sizes actually costing less than a good grade of laboratory tubing. Black pipe made of the same material is also available from the manufacturer, Elmer E. Mills Corp., 2930 N. Ashland Ave., Chicago 13, Illinois.

New Filtration Chart

The new, classroom-size S & S Filtration Chart, published by Carl Schleicher & Schuell Company, gives complete data on relative retention values of S & S Analytical Filter Papers and other brands. It shows at a glance the right paper to use for a given analysis.

The chart itself measures 17 × 22 inches, is printed in 2 colors, and has a laminated plastic surface for protection in the laboratory.

The S & S Filtration Chart is also available in notebook-size reprints for student use.



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Both the classroom-size S & S Filtration Chart and the notebook-size reprints are available without charge or obligation from Carl Schleicher & Schuell Company, Keene, New Hampshire, manufacturers of "High Quality American Filter Papers."

Magnets

A new magnetic material developed by Naval Ordnance Laboratory, White Oak, Maryland, exhibits coercive force of 3000 oersteds, greater than any known permanent magnetic material. It's composed of bismuth and manganese, and magnets can be made by powder metallurgy technique. Production involves heating powdered manganese and bismuth at 700° C., hot-pressing resulting bismuthide at 300° C. in strong magnetic field. Details from Navy Technical News, Office of Information, Navy Department, Washington, 25, D.C.

New Literature

● The Wilkens-Anderson Co., 4525 West Division Street, Chicago 51, Illinois, announces publication of their *Waco Nephelos Notes*, available upon request from the company. This pamphlet features practical applications of nephelometry. The methods mentioned are used by working chemists and bacteriologists.

● An interesting and informative 56-page booklet on High Vacuum Apparatus, recently revised to include new type vacuum connectors, couplings, etc., has just been published by Central Scientific Company. It contains detailed information on planning the high vacuum system together with many valuable tables and charts. Included, also, is complete description of various types of high vacuum apparatus and accessories. A copy of this booklet, Bulletin 10E, may be had without charge by writing Central Scientific Company, 1700 Irving Park Road, Chicago 13, Illinois.

● A new folder describing the "Contours" Portable Photo-copier and its uses has just been released by F. G. Ludwig Associates, Deep River, Connecticut.

The new literature describes in detail, with photographs, how "Contoura" is used. It also lists the many uses to which Contoura-copying can be put. A free copy of this folder is available by writing the manufacturer.

● A 16-page booklet on Orlon laboratory and industrial apparel is available from Worklon, Inc., 253 W. 28th St., New York 1, New York. Included are a number of laboratory reports on the technical properties of Orlon.

● The Blue M Electric Company, 306 W. 69th St., Chicago 21, Illinois, has just published the first bulletin containing complete data on their Con-Wate oven. Included is a discussion of the effect of air weight on oven operation. Copies of the bulletin are available from Blue M Electric.

● The U. S. Stoneware Co. has just released their 16-page Bulletin No. 730, on Tygon paint. This bulletin not only gives a full description of Tygon paint, but also incorporates information on Tygorust, the new vinyl primer, which has created much

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are widely used for the safe handling of glass bottles containing harmful chemicals; also the storage and recovery of expensive serums, biologicals, and other costly products.

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Bulletin No. 730 tells where and where not—how, and how not to use Tygon paint and Tygorust primer. Comprehensive chemical-resistance charts, and an extensive chart on recommended primers and surface treatments should be of great interest to users of industrial corrosion-resistant paints.

Readers can obtain copies of this new bulletin without charge, by writing Mr. G. W. Fine, The U. S. Stoneware Co., Akron 9, Ohio.

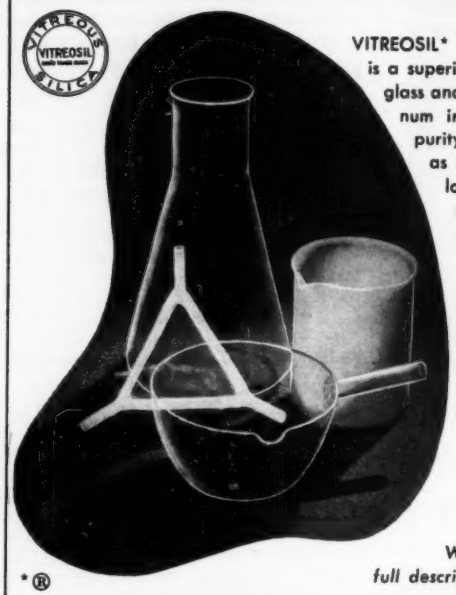
● The Chicago Surgical and Electrical Co. has just issued a bulletin describing their newly designed, complete line of water baths. Copies may be secured upon request to the company at 277 N. Desplaines St., Chicago 6, Illinois.

● A 16-page catalog on liquid-handling equipment has just been published by Ertel Engineering Corp., Kingston 8, N.Y. Several pages are devoted to illustrations and descriptions of laboratory filters and mixers. Copies of Catalog No. 52 are available from the company.

● A new illustrated Beckman Ease catalog describes applications, methods, and features of the EASE Computer. Featured as the lowest-priced quality instrument in its field, this analog computer functions as an equation solver, simulator, or testor.

The EASE Computer is already being used by many industrial research and academic organizations throughout the country. Write Beckman Instruments, Inc., South Pasadena 1, California. Ask for Data File 309-36.

FOR EXACTING LABORATORY USE



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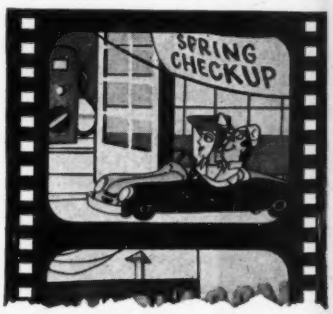

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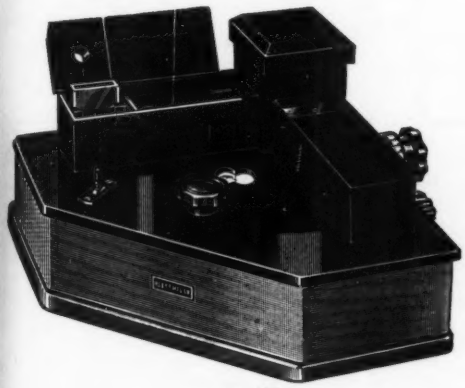

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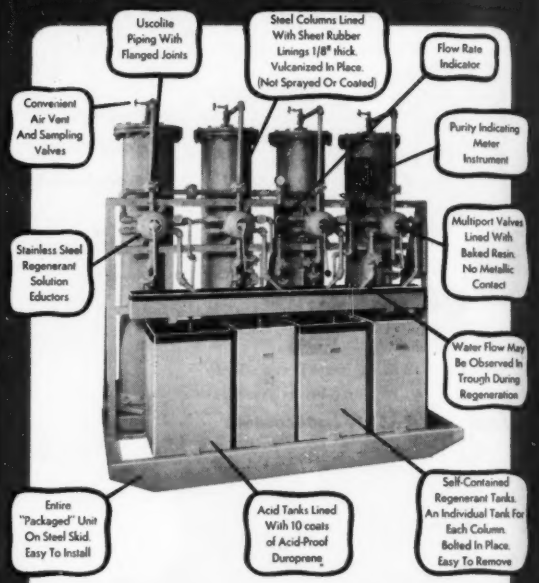
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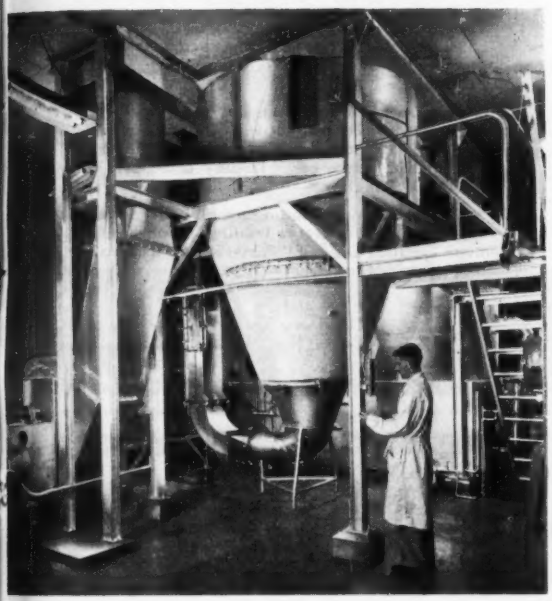

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"To us it seems that the material in Chapters VII and VIII should be combined under the title of the latter, 'Suggestions for Practical Polarography,' for it is in these two chapters that there are presented many useful manipulative techniques and trouble shooting procedures which are very rarely found conveniently collected in one volume and which generally must be learned through more or less painful experience. Included are methods of measuring wave height and translating it into units of concentration; criteria for the selection of supporting electrolytes; use of the compensator; determination of half wave potential; pH measurement with the dropping mercury electrode; use of the literature; causes of erroneous results; and selection and calibration of electrode capillaries. An appendix lists useful data, buffer compositions and a brief bibliography of general polarographic texts and published bibliographies. A thorough index permits ready location of subject matter.

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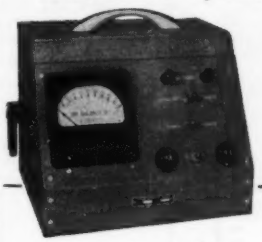

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Linde & Rogers J. CHEM. ED. Pgs. 28, 576-577. Instrumental Methods of Analysis, 114-115, 119. Willard, Merritt & Dean, Van Nostrand, 1949.

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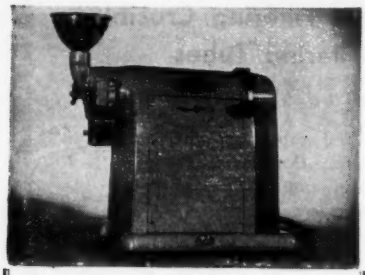

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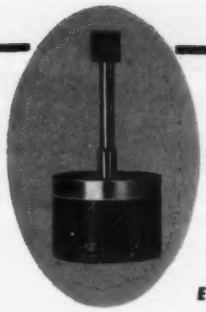

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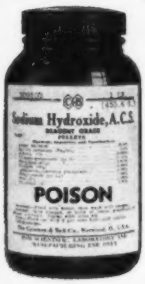

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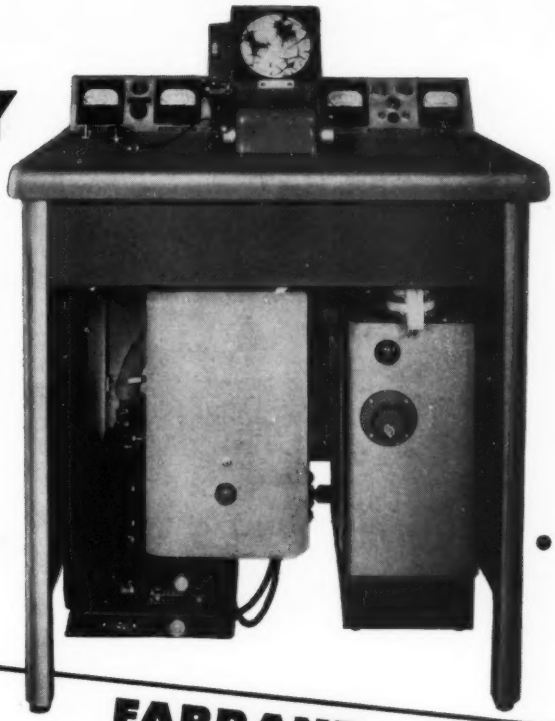

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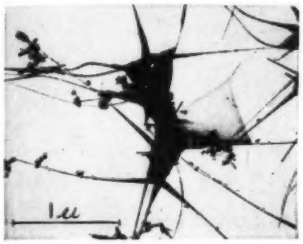

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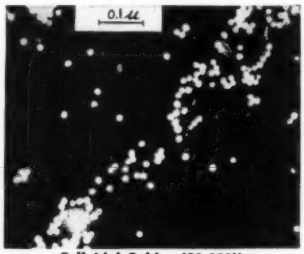

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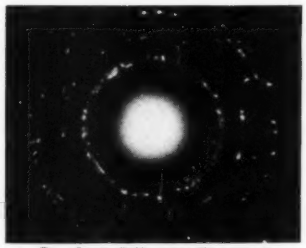

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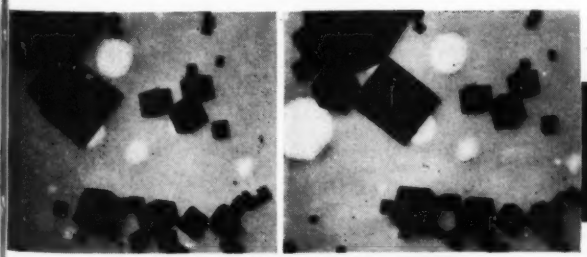

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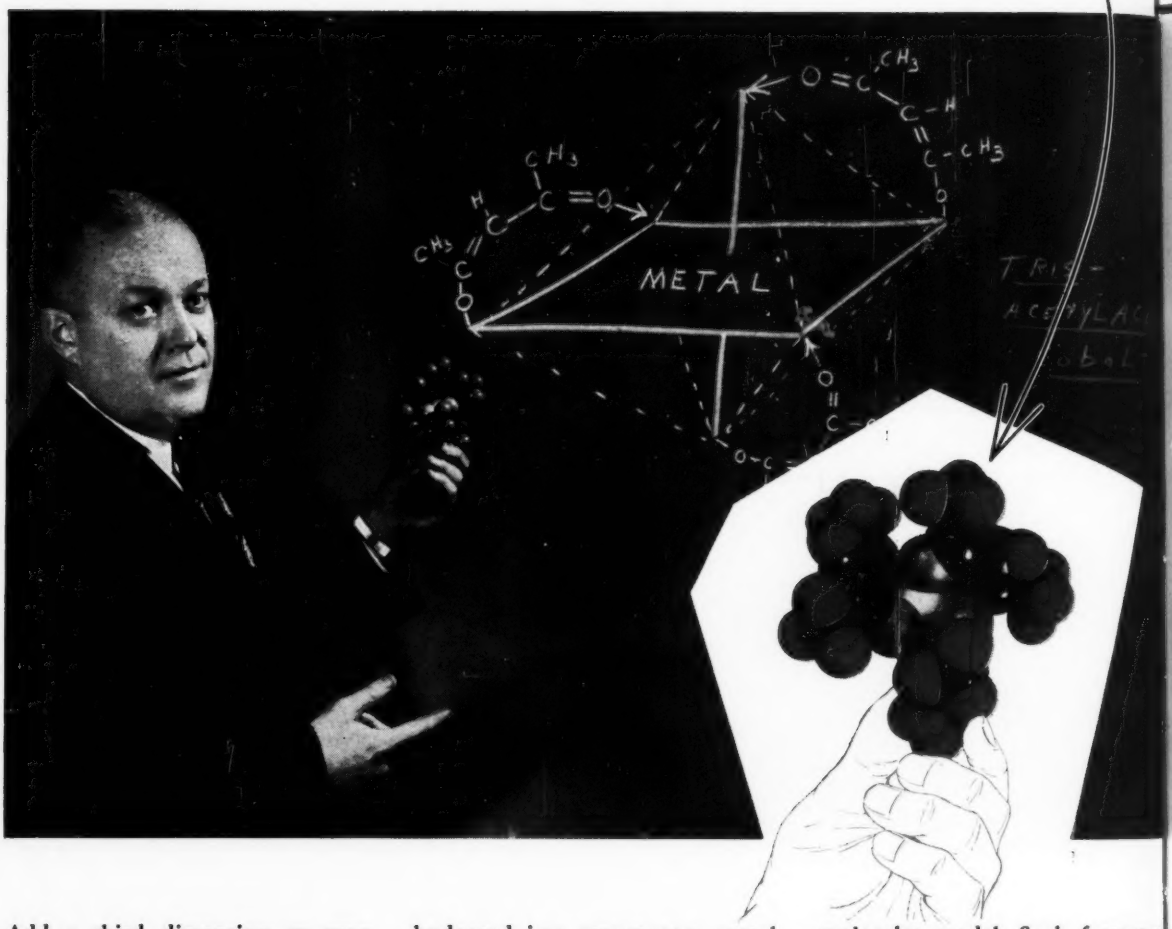

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